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Review of physical vapor deposited (PVD) spectrally selective coatings for mid- and high- temperature solar thermal applications

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Abstract

Solar energy is the most abundant source of renewable energy. The direct method of harnessing solar energy is the solar thermal conversion method using solar absorbers. The absorbers are coated with solar selective coatings with high absorptance and low thermal emittance. Spectrally selective coatings which are stable up to temperatures ≤ 300°C (in air and vacuum) have been developed in the past. These coatings are mainly deposited from wet chemical routes (e.g., electrodeposition) and have been reviewed widely in the literature. Because of the environmental issues as well as low thermal stability of these wet chemical deposited coatings, researchers all over the world started looking for other alternative routes such as physical vapor deposited (PVD) coatings. A great deal of research has been carried out since 1990s to develop PVD coatings for both mid- and high- temperature applications. The mid-temperature coatings are used mainly for solar hot water and industrial process heat applications, whereas, the high- temperature absorber coatings are used in concentrating solar power systems for solar thermal power generation. It is well recognized that in order to increase the efficiency of solar thermal power plants, solar selective coatings with high thermal stability are required. In recent years, significant efforts have been made in the field of solar selective coatings to achieve high solar absorptance and low thermal emittance at higher temperatures (T ≥ 400°C). Transition metal based cermets have emerged as novel high temperature solar selective coatings, which are currently being used for solar thermal power plants for electricity generation. Solar selective coatings based on transition metal nitrides, oxides and oxynitrides also hold great potential for high- temperature applications because of their excellent mechanical and optical properties, which are yet to be commercialized. In this review, we present the state-of-the-art of the physical vapor deposited solar selective coatings used for solar thermal applications with an

emphasis on sputter deposited coatings for high- temperature applications. A detailed survey, covering the period 1970-present, has been made for the PVD deposited solar selective coatings with high absorptance and low emittance. This review article also describes in detail about the commercially available PVD coatings for flat-plate/evacuated tube collectors and solar thermal power generation applications.

Key words: Mid- temperature solar selective coatings; high- temperature solar selective coatings; physical vapor deposition; sputtering; evaporation; concentrated solar power.

1. Introduction

In recent years, renewable sources of energy have gained increased attention due to the depletion of fossil fuels, increasing concentration of green house gases and climate changes. In the next 50-100 years, reduction of greenhouse gases of about 50% throughout the world is required [1]. In order to reduce greenhouse gases, we need to use renewable energy sources, and solar energy is one of the most environmentally safe energy sources. The simplest and most direct method of harnessing solar energy is solar thermal conversion method.

Solar energy is converted into thermal energy using a special kind of heat exchanger known as a solar collector. Solar collectors can be classified into two general categories: (i) non-concentrating and (ii) concentrating. In the non-concentrating type, the collector area (the area that intercepts the solar radiation) is the same as the absorber area (the area that absorbs the radiation) [2]. Flat plate collectors and evacuated tube collectors are non-concentrating type collectors. These collectors are mainly designed for solar hot water and industrial process heat applications and are described elsewhere [2-4]. These collectors use both diffuse and direct beam solar radiation and do not require tracking of the sun. They are mechanically simpler than concentrating collectors and require less maintenance [2]. Spectrally selective coatings used in solar collectors are known to enhance the efficiency of photothermal conversion. The use of spectrally selective coatings on solar collectors was proposed by Tabor, Shaffer, Gier and Dunkle and others in 1955 [5-8]. The first absorber coatings successfully applied to flat plate collectors were electrodeposited black nickel, NiS-ZnS composite, black chrome and chemically converted black copper oxide [5,8]. Since then, a wide range of selective surfaces were developed by wet chemical methods (electrodeposition [9,10], electroless deposition [11,12], anodization [13,14], chemical conversion [15,16], sol-gel [17,18,19], thickness sensitive

spectrally selective paints [20,21,22], thickness insensitive spectrally selective paints [23,24,25], solution growth [26,27], spray pyrolysis [28,29], etc.), and have been reported and reviewed widely in the literature [30-34]. Among these, electrodeposited black chrome coatings have been widely studied and used for solar hot water applications [35,36]. Solar selective coatings obtained from wet chemical methods do not exhibit higher chemical and thermal stability. In addition, these processes are not environmentally friendly. Due to these reasons, physical vapor deposited (PVD) solar selective coatings have been explored as alternatives for wet chemical deposited coatings [37-41]. Literature survey indicates that a comprehensive review of PVD deposited solar absorber coatings is lacking and it is necessary as the PVD processes are environmentally friendly and hold a great promise to design the solar absorber coatings with desired properties mainly for mid- and high- temperature applications.

A large number of mid- and high- temperature solar selective coatings have been developed by PVD methods such as evaporation, ion plating, pulsed laser deposition, cathodic arc evaporation and sputtering since 1970s [30]. Amongst these, magnetron sputtering method has been widely used for large-area deposition of solar selective coatings. Coatings which are thermally stable in the range of 100-400°C are called mid- temperature solar selective coatings and coatings stable above 400°C (in air and vacuum) are called high- temperature solar selective coatings. The mid- temperature solar selective coatings are used for industrial process heat, desalination and solar hot water applications. Whereas, the high- temperature absorber coatings are used in concentrating solar power (CSP) systems for solar thermal power generation [3,4]. Various types of non-concentrating and concentrating collectors are shown in Figure 1. The concentrating type collectors can be categorized as: central receiver, parabolic trough collector (PTC), linear Fresnel collector and parabolic dish collector. In CSP systems, various types of

mirrors, reflectors or concentrators are used to concentrate the solar energy and they provide higher temperatures (i.e., 400–1000°C) than non-concentrating type collectors [42]. The CSP systems are used to generate electricity and produce very low levels of greenhouse-gas emissions. Due to this, the CSP systems are emerging as a key technology for extenuating climate change. Unlike solar photovoltaic technologies, CSP in conjunction with suitable heat-transfer fluid (viz., molten salt) has the capacity to store heat energy for short periods of time for later conversion to electricity [43]. According to the International Energy Agency (IEA) report, by 2050, the CSP systems could provide 11.3% of global electricity with 9.6% from solar power and 1.7% from backup fuels (i.e., fossil fuels and biomass) [43].

For solar thermal power generation, at present, parabolic trough technology is the most proven and low cost, large-scale solar power technology. Compared to other solar technologies, parabolic trough systems have the advantage of being established as a technology for installation at a commercial level. The first trough plant was installed in the USA in 80's. Since then, they have undergone vast improvements both in terms of cost and efficiency. Parabolic trough systems currently have an installed capacity of 870 MW, with 2152 MW under construction and 10 GW in development [44,45]. A detailed and recent review of parabolic trough solar collectors and their applications have been reported by Fernandez-Garcia et al. [46]. Parabolic trough collectors use an evacuated receiver tube to convert sunlight to thermal electric power. A heat-transfer fluid (i.e., synthetic oil, molten salt - 60%KNO_3+40%$NaNO_3$) is circulated in the receiver tubes and the fluid is heated to ≥ 400°C by the concentrated solar radiation. The heated fluid is pumped through a series of heat exchangers to produce superheated steam. The steam is then converted into electrical energy in a conventional steam turbine generator. So, the evacuated receiver tube is the heart of the parabolic trough collector. The evacuated receiver

tubes are coated with high- temperature solar selective coatings in order to enhance the efficiency of photothermal conversion. For parabolic trough collector applications, the spectrally selective coatings should have high absorptance (α) and low emittance (ε) at higher operating temperatures ($T > 400°C$) in air and vacuum.

In this review article, we have focused on physical vapor deposited solar selective coatings used for mid- and high- temperature solar thermal applications. The outline of the review article is as follows: Section 1 gives an introduction about the need for renewable energy, different types of non-concentrating and concentrating systems and the need for solar selective coatings as discussed above. Section 2 outlines the different types of solar selective coatings. Sections 3 and 4 are more specific and provide a detailed survey of physical vapor deposited mid- and high- temperature solar selective coatings for flat plate/evacuated tube and solar thermal power generation applications. We have also discussed about the commercially available mid- and high- temperature solar selective coatings in Sections 3 and 4, respectively. Sections 5 and 6 present the outlook of mid- and high- temperature spectrally selective coatings and conclusions, respectively.

2. Spectral selectivity mechanisms

The first known flat plate collector was developed by Horace de Saussure in 1767 and later used by Sir John Herschel [47]. In 1908, William J. Bailey invented a collector with an insulated box and copper coils [47]. This collector design is very similar to the present design. The research on spectrally selective absorber surfaces for solar collectors was pioneered by Tabor in 1955 and later carried out by several other researchers [5-8]. Tabor proposed two different concepts for developing solar selective surfaces. The first type constitutes a low-emissivity metal base covered by a thin surface layer such as black chrome, black nickel, copper

oxide, etc., which is non-transparent in the visible region but substantially transparent in the infrared region. The second type consists of metallic systems with low emissivity which exhibit high absorptivity in the visible spectrum due to color or a finely divided structure [8]. However, the major growth of the research on solar absorber coatings started in late 1970s after the oil crisis in 1973. In the following years, several mechanisms have been employed for the development of spectrally selective surfaces. An ideal spectrally selective absorber has zero reflectance in the visible region and high reflectance in the infrared region. Various transition metals and semiconductors show such selective characteristics, but their compositions need to be modified greatly to achieve the ideal characteristics. In order to achieve the spectral selectivity, the absorber coatings need to be designed suitably. Various spectrally selective coatings have been designed based up on the following concepts: (i) intrinsic absorber (e.g., HfC, MoO_3 doped Mo, ReO_3, etc.) [48,49] (ii) metal-semiconductor tandem (or) absorber-reflector tandem [48] (iii) heat mirror (or) selectively solar-transmitting coating on a blackbody absorber (e.g., indium tin oxide on silicon) [50,51] (iv) multilayer absorber (e.g., Al_2O_3/Mo/Al_2O_3) [48] (v) textured surface [52-54] and (vi) metal-dielectric composite/cermet (e.g., Cr-Cr_2O_3, SS-AlN, etc.,) [55-58]. Detailed discussions about the different types of spectrally selective coatings can be found in the literature [30,31,32,47,48].

All these above mentioned concepts have been used to develop various mid- and high-temperature solar selective coatings. But the most widely used concepts are metal-dielectric composites, multilayer absorber and absorber-reflector tandem and the coatings developed using these concepts are discussed in Sections 3 and 4.

3. Survey of mid- temperature PVD solar selective coatings

A large number of physical vapor deposited low- and mid- temperature solar selective coatings have been developed in the past [30,31,32,34]. Even though the scope of this article is limited to mid- and high- temperature physical vapor deposited solar selective coatings, we have presented a few important low- temperature solar selective coatings in the beginning of this section, which formed the basis for the development of mid- and high- temperature solar selective coatings. We also describe a few important mid- temperature solar selective coatings developed by evaporation and sputtering methods. At the end of this section, we discuss about the commercially available physical vapor deposited solar selective coatings.

3.1. Evaporation

The evaporation method (thermal and electron beam) has been used for several years to develop highly absorptive films and also to produce fine particles of many materials [59-63]. Generally, metals have low absorptance in the solar spectrum region and low emittance in the infrared region. The reflectance of the metals in the visible region is reduced drastically by depositing a semiconductor absorber layer on top of the metal. This approach was first studied by Hass et al. [64]. They have deposited germanium on top of aluminum substrate and reduced the reflectance of opaque aluminum from 90% to 40% at 430 nm. Further addition on SiO on top of the Ge coating resulted in zero reflectance at 600 nm.

Similarly, Mattox and Kominiak used various narrow band gap semiconductors (i.e., Si, Ge and PbS) as solar selective absorbers because they absorb in the solar spectrum and are transparent in the infrared region [65]. They investigated the effect of surface morphology on the absorptance of Si, Ge and PbS coatings. It was observed that coatings with high absorptance have a very rough surface morphology when compared to the reflecting coatings. Absorptance

greater than 0.95 was obtained for Ge and PbS coatings, whereas, Si coatings exhibited very low absorptance (0.70). The emittance values of the Ge ($\varepsilon_{240°C}$ = 0.48) and PbS ($\varepsilon_{240°C}$ = 0.14) coatings were also very high resulting in very low solar selectivity [65]. Semiconductor solar absorbers with high solar selectivity were developed by Peterson and Cocks by angular vapor deposition of Te and Se on various metal substrates [66,67]. Tellurium coatings deposited on Au, Al and Cu substrates exhibited absorptance in the range of 0.90-0.92 and emittance in the range of 0.03-0.06 at 100°C. McMohan and Jasperson also developed PbS solar selective absorbers without any antireflection coating (ARC) on Al substrates, which exhibited high solar selectivity [68]. High solar absorptance (0.95) was achieved for 100 nm thick PbS coating as compared to Si and Ge, where the optimum thickness was in the range of 1-10 μm. The reduction in film thickness for PbS is due to its large absorption coefficient when compared to Ge and Si. Furthermore, PbS is a direct bandgap semiconductor, whereas Ge and Si are indirect band gap semiconductors. The high solar selectivity of the PbS coatings has been attributed to a unique surface morphology, which reduces the front surface reflection [68]. They have reported that such unique surface morphology does not obey the Fresnel equation for a simple dielectric-air interface. The effect of PbS film thickness on the absorptance and emittance of the coatings was investigated by Marchini and Gandy [69]. They have demonstrated both theoretically and experimentally that the optimum coating thickness to achieve high solar selectivity is in the range of 300-800 Å. Unfortunately, all semiconductor materials have high refractive index, which resulted in high front surface reflection [65,70]. In order to reduce the front surface reflection, an antireflection coating must be deposited on top of the semiconductor layer. Flordal and Kivasi developed Ge and PbS semiconductor solar absorbers with silicon monoxide antireflection coating on different metal substrates (i.e., Al, Ni and Cr) [71]. Ge-SiO and PbS-

SiO coatings deposited on various metal substrates (Al, Ni and Cr) exhibited absorptance in the range of 0.79-0.94 and emittance in the range of 0.01-0.11 at 127°C. Martin et al. prepared PbS thin films with ZrO_2 antireflection coating by different routes such as ion beam sputtering, electron beam evaporation and thermal evaporation and compared the optical properties of these coatings [72]. Thermally evaporated PbS coatings exhibited very high absorption when compared to the sputtered and electron beam evaporated coatings. This is due to the porous surface texture of the thermally evaporated coatings [72]. The thermal stability of the above mentioned coatings have not been reported.

Like metal blacks and semiconductors, various cermet coatings have also been developed by the evaporation method [37-40]. G.L. Harding developed evaporated black chrome as an alternative for electroplated black chrome coatings [37]. He reported that the evaporated black chrome exhibited an absorptance of 0.80 and an emittance of 0.05 at 100°C with thermal stability of 200°C in vacuum [37]. Even though black chrome coatings have been in use for several years, their properties were poorly understood until they were studied by Granqvist and Niklasson [38]. They were the first to report the optical properties of ultrafine chromium particles prepared by evaporation method. The spectral selectivity of these coatings is comparable to that of the best electroplated black chrome coatings [38]. The ultrafine chromium particles exhibited high absorptance in the solar spectrum and low emittance in the infrared region [73]. The optical properties of the chromium films deposited at an oblique angle of incidence were studied by Kivasi [39]. The coating consists of a high concentration of metallic chromium surrounded by a very thin film of chromium oxide. Unlike gas evaporation (i.e., evaporation of chromium in the presence of oxygen) or co-evaporation (evaporation of chromium and its oxide), the chromium oxide formation in this coating is due to residual oxygen

gas present in the vacuum chamber. This coating exhibited high absorptance in the solar spectrum and was transparent in the infrared region.

Niklasson and Granqvist developed a single layer Co-Al_2O_3 cermet with Al_2O_3 antireflection coating by vacuum co-evaporation of Co and Al_2O_3 [74]. Absorptance of 0.94 and emittance of 0.04 at 100°C have been obtained for an optimized coating having 70 nm of Co-Al_2O_3 with a higher Co metal volume fraction of 0.60 on a Ni or Al reflector with a 70 nm Al_2O_3 antireflection coating. The high absorptance was achieved without composition grading and surface roughening. In order to achieve absorptance greater than 0.90, graded and double layer cermet concepts were used by several researchers [55,58]. From numerical modeling calculations, Zhang and Mills reported that the Co-Al_2O_3 double layer cermet structure exhibits better solar absorptance and emittance than single layer Co-Al_2O_3 cermet [75]. The temperature dependence of the photothermal conversion efficiency with four different concentrations for the Co-Al_2O_3 cermet coatings is shown in Figure 2. It is clearly evident from the figure that the Co-Al_2O_3 cermet coatings exhibit high photothermal conversion efficiency with concentration factors of 8 to 10. Various cermet coatings such as Au-Al_2O_3, Ag-Al_2O_3, Cr-Al_2O_3, Cr-Spinel and Cu-Spinel have also been developed for evacuated tube collectors applications [76]. Absorptance greater than 0.90 and emittance less than 0.05 at 100°C were achieved for these coatings. The high absorptance was achieved by grading the composition of the cermet coatings. Among these cermets, Cr-Al_2O_3 cermet is the best candidate for CSP applications because of its good thermal stability in vacuum (i.e., 500°C for 100 h) [76]. The main drawback of the evaporation method is that it is not suitable for large area deposition of solar selective coatings due to poor growth rate control and presence of large number of pin holes.

3.2. Cathodic arc evaporation

Cathodic arc evaporation method has been widely used to deposit a variety of metallic and compound thin films for various applications (such as wear resistance, corrosion resistance and decorative) [77]. But only a very few papers are available in the literature for the development of solar selective coatings using cathodic arc evaporation method [78-80]. This is because the cathodic arc method has one major disadvantage: i.e., the emission of macro particles of cathodic metal, which influences the optical properties of the coatings [77]. Yin et al. used this method and prepared Al-AlN and a-C:H-SS cermet coatings on silicon and glass substrates [78]. The homogeneous Al-AlN cermet with AlN antireflection coating deposited at unfiltered condition exhibited an absorptance of 0.90 and emittance of 0.06 at room temperature. Whereas, a-C:H-SS cermet with a-C:H antireflection coating deposited at macroparticle filtered condition exhibited very low reflectance in the visible region [78]. Jahan and Smith prepared Ag/TiO_2 cermets with angular and spectral selectivity of optical transmittance [79]. TiO_2 coatings were deposited by oblique angle deposition using a filtered cathodic arc and in a magnetron sputtering system. The metallic Ag was co-deposited by thermal evaporation. They have reported that the cathodic arc evaporated coatings showed better solar selective results than the sputtered coatings. This is due to the different microstructure of the oblique oxide obtained from cathodic arc evaporation. Similarly, Marquez et al. prepared CuO coatings by cathodic arc with absorptance of 0.93 and emittance of 0.16 at 300°C on steel substrates [80]. The cathodic arc evaporated CuO coating exhibited solar selectivity of 5.8, which is in good agreement with the sputter deposited CuO coatings ($\alpha/\varepsilon = 7.5$) [80,81].

3.3. Sputtering

Sputtering is a widely used method for large area deposition of solar selective coatings. Fan and Spura developed sputter deposited chromium oxide cermet coating and compared with electrodeposited black chrome coating. They found that the electrodeposited coatings are actually Cr-Cr_2O_3 cermets comparable in composition and microstructure to the sputtered films. The sputter deposited Cr-Cr_2O_3 cermet with Cr_2O_3 antireflection coating deposited on nickel coated stainless steel (SS) substrates exhibited α/ε(100°C) of 0.92/0.08 [40,41]. The Cr-Cr_2O_3 cermet was prepared by radio frequency (RF) sputtering using a hot-pressed target containing 71 vol% Cr_2O_3 and 29 vol% Cr. The coatings were thermally stable in air at 300°C for 64 h. The measured reflectivities of as-deposited and heat-treated cermet coatings are shown in Figure 3. Further increase in the temperature (i.e., 400°C for 60 h) resulted in delamination of the coating from the substrate due to differences in the thermal expansion coefficients. Cr-Cr_2O_3 coatings were also developed using various other concepts such as graded cermets, multilayer cermets and multilayer absorbers, which are discussed below [82-84].

Graded Cr-Cr_2O_3 cermets deposited on Cu and Al substrates by gradually changing the oxygen flow rate exhibited high absorptance in the range of 0.90-0.94 and low thermal emittance of 0.04 at 100°C [82]. Recently, our group developed Cr_xO_y/Cr/Cr_2O_3 multilayer absorber coating for mid- temperature solar thermal applications [83]. The Cr targets were sputtered using asymmetric bipolar pulsed direct current (DC) generators in Ar+O_2 and Ar plasmas to deposit the multilayer absorber coating. The optimized multilayer absorber coating exhibited high absorptance (0.89-0.91) and low thermal emittance at 82°C (0.05-0.06) on Cu substrates. The coatings were thermally stable in air at 300°C. At higher temperatures, the absorptance

decreased and the emittance increased drastically which was due to the oxidation of Cr crystallites, increased surface roughness and the formation of CuO. The change in the oxidation state of metallic Cr and the formation of CuO were confirmed by X-ray photoelectron spectroscopy (XPS) data, which is shown in Figures 4(a) and (b), respectively. The coatings were also found to thermally stable in vacuum at 600°C for 2 h. Accelerated aging tests indicated that the coatings deposited on Cu substrates were stable in air up to 250 h at 250°C [83].

Yin et al. have developed Cr-Cr_2O_3 multilayer cermets (with low-high-low metal volume fraction profile) using the target current as a control parameter in the optimization [84]. The solar absorptance of the sputtered black chrome selective surface is in the range of 0.92-0.96 and the thermal emittance is 0.05-0.08 at 100°C. The coatings were thermally stable at 300-400°C for 1 h and the corresponding reflectance spectra measured at different temperatures are shown in Figure 5. Long time aging at 170°C suggested that the coatings are suitable for solar hot water applications [84]. The electrodeposited black chrome and sputter deposited Cr-Cr_2O_3 coatings are useful for solar water heating applications. In evacuated tubes, the black chrome coatings have also been used for steam generation at low pressures, wherein the application temperature is around 300°C [85,86]. However, for high- temperature applications these coatings are not recommended since they undergo compositional changes. Similar to graded Cr-Cr_2O_3 cermets, graded Cu-Al_2O_3 cermets were developed for evacuated tube collector applications [87]. The graded Cu-Al_2O_3 cermet coatings exhibited absorptance in the range of 0.86-0.90 and emittance of 0.03 at room temperature. Annealing of the coatings in vacuum at 300°C resulted in a decrease in the solar absorptance from 0.86 to 0.83. This coating can therefore be used only for

low- and mid- temperature solar applications. Recently, our group developed Ag-Al_2O_3 based nanocermets for mid- temperature solar thermal applications [88]. The optical properties of the nanocermets are due to surface plasmon resonance, which is attributed to collective oscillations of conduction electrons of noble metal nanoparticles embedded in a dielectric matrix. The optical properties of the nanocermets can be judiciously controlled by controlling the particle size, shape, concentration of particle in matrix, particle distribution and local dielectric environment of the host matrix. These coatings exhibited a solar selectivity of 0.94/0.04 on Cu substrate, but low thermal stability (up to 250°C in vacuum) [88].

G. L. Harding developed various transition metal carbide and silicide coatings for solar thermal applications [89,90]. The metal silicides and carbides of chromium, iron, molybdenum, nickel, stainless steel, tantalum, titanium and tungsten were deposited by reactive sputtering on bulk and sputtered copper substrates [89-91]. The metal silicide coatings were also deposited on evaporated Ni and bulk stainless steel substrates. A solar absorptance of 0.76-0.80 and a thermal emittance of 0.02-0.03 were observed at room temperature for the homogeneous metal carbides prepared on bulk copper. Similarly, the homogenous metal silicides on bulk copper have α = 0.75-0.81 and ε = 0.02-0.03 at room temperature. These coatings were thermally stable at 400°C in vacuum. The absorptance values of the metal silicides deposited on sputtered copper, evaporated nickel and bulk stainless steel substrates are enhanced due to the low visible reflectance of these substrates. Stainless steel silicide exhibited high absorptance of 0.87 and low thermal emittance of 0.04 at room temperature on evaporated Ni. Whereas, the stainless silicide deposited on bulk copper substrate exhibited absorptance of 0.81 and emittance of 0.02 at room temperature. The coatings deposited on bulk and sputtered copper substrates exhibited different aging effects. No deterioration was observed after 250 h at 250°C and 120 h at 400°C

in air for the films on bulk copper, whereas, the coatings deposited on sputtered copper began to deteriorate slightly at 250°C. The absorptance of the homogeneous metal carbide and silicide coatings was increased by grading the coating composition, i.e., the coating was highly metallic near the substrate and dielectric at the air-film interface. These graded metal carbide and silicide coatings exhibited absorptance in the range of 0.90-0.95 without affecting the emittance [92].

Various graded metal carbide coatings such as SS-C, Cu-C, Cr-C, Fe-C etc., were developed for evacuated tube collector applications [92-98]. One of these coatings, i.e., SS-C has been successfully commercialized and was marketed by Nitto Kokhi, Japan [99]. These coatings were deposited on glass absorber tubes for evacuated tube collectors using cylindrical magnetron post cathode batch coating systems [92]. The graded SS-C coating was deposited by reactive sputtering of the SS cathode in argon and acetylene plasma. The flow rate of acetylene was sequentially increased from zero to maximum during the deposition. This results in grading of film stoichiometry from pure stainless steel at the substrate surface to dielectric SS-C at the top surface. The graded SS-C coatings exhibited an absorptance of 0.93 and emittance of 0.04 at room temperature. Both homogeneous and graded SS-C coatings were stable up to 300°C in vacuum for 2000 h. The optical measurements and the Auger electron spectroscopy results of as-deposited and vacuum annealed SS-C coatings clearly showed that the degradation caused is mainly due to two mechanisms: (i) oxidation of the metal rich layers of the metal-carbon film and (ii) diffusion of metal components into the substrate [100]. G.L. Harding also demonstrated that deposition of a thin coating of carbon particles (i.e., a-C:H) on top of the absorber layer increased the absorptance by 2% with 1% increase in the emittance [95]. The effect of various antireflection films (i.e., Al-C-F, Al-C-O and Si-O) on graded stainless steel carbide surfaces clearly showed that the absorptance of the coatings can be increased by 4%

with 1% increase in the emittance. Wyon and Valignat developed a Cu/SS/a-C coating by successively depositing an opaque Cu layer, a thin film of stainless steel and an amorphous carbon layer by non-reactive magnetron sputtering [101]. This coating exhibited absorptance higher than 0.90 and emittance less than 0.05 at 300°C. The coatings were thermally stable in vacuum at 400°C for 4 h [101]. The interdiffusion between the layers and the outward diffusion of Cu and its subsequent oxidation resulted in degradation of the coatings at higher operating temperatures. Recently, Juang et al. developed SS/SS-N coating by sputtering a single stainless steel target in Ar and Ar+N_2 plasmas. This coating exhibited an absorptance of 0.91 and emittance of 0.06 at 82°C. The thermal stability of the coating has not been reported [102].

G. L. Harding also developed a multilayer SS-C coating using the multilayer absorber concept (i.e., dielectric/metal/dielectric design concept). A thin SS metal layer (approximately 8-20 nm thick) was stacked between two dielectric SS-C layers to produce the multilayer absorber [103]. He has developed three and five layer stainless steel carbide coatings on copper coated glass slides. The multilayer SS-C coatings exhibited high absorptance in the range of 0.94-0.95 and emittance of 0.05-0.06 at room temperature, when compared to graded SS-C coatings ($\alpha = 0.92$; $\varepsilon < 0.04$). The increase in the absorptance and emittance values of the multilayer SS-C coatings was due to the increased thickness of the absorbing layer, which resulted in a wider absorption band. Harding et al. also designed a number of new solar selective coatings by computer simulation and developed the same by sputtering method [104,105]. These coatings have been produced using continuously graded or multilayer films of reactively sputtered aluminum-carbon-fluorine, aluminum-carbon-oxygen or aluminum-nitrogen composite materials as the absorbing layer and pure aluminum as the low emittance metal base layer. These coatings exhibited absorptance in the range of 0.93-0.97 and emittance

in the range of 0.05-0.08 at room temperature and were thermally stable in air at 500°C for 1 h. Sputter deposited AlN solar selective coatings have also been studied by other researchers [104-107]. Zhiqiang and Harding used a cylindrical DC magnetron sputter coater to deposit the AlN coatings onto batches of solar collector tubes [105]. A single aluminum cathode was used for the deposition of these coatings [105]. An optimization study of Al-AlN cermet coatings using a numerical model was reported by Q. C. Zhang [106]. The studies revealed that an optimized ten layer graded film and a three layer cermet coating exhibited identical absorptance (0.95), emittance (0.05 at 80°C) and photo-thermal conversion efficiency. The optimized three layer cermet coating consists of an antireflection coating and two cermet layers with metal volume fractions of 0.093 and 0.255. It is clear that the SS-C and AlN cermet coatings can be used for only low- and mid- temperature applications due to their poor thermal stability. Table 1 shows the absorptance, emittance and thermal stability of various physical vapor deposited mid-temperature solar selective coatings.

3.4. Performance criterion evaluation

In addition to high solar absorptance and low thermal emittance, long term thermal stability is also very important for spectrally selective coatings used in the flat plate/evacuated tube collectors. A procedure for accelerated life testing of solar absorber surfaces was developed within the framework of the working group, "Materials in Solar Thermal Collectors" of the International Energy Agency-Solar Heating and Cooling program [108-112]. The procedure was formulated as a standard and submitted to International Organization for Standardization (ISO). It carries the designation ISO/CD 12592,2 '*Solar Energy – Materials for flat-plate collectors – Qualification test procedures for solar surface durability*'. The proposed standard describes in detail, the procedure for the examination of the long-term stability of solar absorber coatings

used in flat-plate collectors for domestic hot water systems. Possible degradation caused by the thermal load, condensation, high humidity and air pollutants (sulphur dioxide) has been taken in to account while formulating the procedure. For estimating the acceptable service life time of an absorber coating, the International Energy Agency-Solar Heating and Cooling program, Task X [108-112] has defined a performance criterion (PC) function for flat plate collector absorber testing. The PC describes the influence in the change of solar absorptance ($\Delta\alpha$) and emittance ($\Delta\varepsilon$) on the solar fraction:

$$PC = -\Delta\alpha + 0.25\Delta\varepsilon \leq 0.05.$$

An absorber surface is qualified if it fulfills the performance criterion for a service lifetime of at least 25 years. Several papers have been published describing the procedure for thermal stability tests according to the International Energy Agency-Solar Heating and Cooling program recommendations [108-111]. The thermal stability test consists of an initial test at 250°C for 200 h followed by an adhesion test. The sample is qualified without further tests if the PC is ≤0.015 and surface adhesion is 0.15 MPa after the initial test. Otherwise, additional tests are required at different temperatures, which are shown in the Table 2.

3.5. Commercially available mid- temperature solar selective coatings

A large number of mid- temperature physical vapor deposited solar selective coatings have been developed, but only few of them have been successfully commercialized. SS-C, SS-AlN, CrN-Cr_2O_3, eta plus, TiNOX, a-C:H/Cr, TiC/TiO_xN_y/AlN and Ni-NiO coatings are commercially marketed by Nitto Kohki, Turbosun, Alanod Solar, BlueTec, Almeco-TiNOx, Ikarus Coatings, Plasma and S-Solar, respectively and are discussed below. Table 3 gives a list of commercially available sputter deposited coatings for mid- temperature applications.

Using the double layer cermet concept, Zhang et al. developed SS-AlN coatings by DC magnetron sputtering of SS and Al targets in Ar+N_2 plasma [113-115]. The nitrogen gas partial pressure was 2.0×10^{-2} Pa. The excellent nitriding resistance of stainless steel and the low nitrogen partial pressure resulted in the deposition of a nearly pure SS layer. A multi-sublayer system consisting of alternating SS and AlN sublayers was deposited by substrate rotation. The thicknesses of the SS and AlN sublayers were less than 2 nm. The structure of the double layer cermet coating consists of a low metal volume fraction (LMVF) cermet layer placed on top of a high metal volume fraction (HMVF) cermet layer. An aluminum nitride antireflection coating was deposited on top of the cermet layers. The SS-AlN coating exhibited absorptance in the range of 0.93-0.96 and emittance of 0.03-0.04 at room temperature. These coatings were thermally stable in vacuum at 500°C for 1 h. Figure 6 shows the reflectance spectra of as-deposited and heat-treated SS-AlN coatings. It is clearly evident from the spectra that the reflectance values in the solar radiation wavelength range were slightly changed due to vacuum annealing and no change in the nature of the spectra beyond 2.5 μm was observed. Even though the coatings have high thermal stability in vacuum (350-500°C), these coatings are mainly used for evacuated solar water collector applications. TurboSun, China in conjunction with Peking University, China and the University of Sydney, Australia have commercially developed evacuated solar collector tubes incorporating sputtered SS-AlN cermet solar selective coatings [114]. Currently, TurboSun manufactures three different series of solar collector tubes with superior solar performance in China. TurboSun also designs, manufactures and installs utility-scale solar hot water systems. TurboSun in China has produced 3.5 million commercial U-shaped all-glass evacuated solar collector tubes for low temperature solar hot water collectors. These tubes are widely used for solar hot water and steam heater applications. According to the

IEA Report, China is leading the solar water collector market (87.5 GW installations) and the dominant collector type is the evacuated tube collector, which represents 54.2% of the global market followed by the flat-plate collector with a market share of 32.6% [4].

CrN/Cr_2O_3 coating with absorptance greater than 0.93 and emittance of 0.07 at 100°C has been developed using experimental design methods [116]. The graded cermet based on chromium oxynitride was deposited on Cu substrates by DC magnetron sputtering technique. The durability tests were carried out as an inter-laboratory comparison in the framework of the working group 'Materials in Solar Thermal Collectors (MSTC)' of the Solar Heating and Cooling (SHC) Program of the International Energy Agency (IEA). The results showed that the graded CrN/Cr_2O_3 coating deposited on Cu sheets is durable enough for an application in ventilated flat plate collectors for domestic hot water system with a service life time of more than 25 years [116]. These coatings were commercially produced by Alanod Solar, Germany and the product name is Sunselect® [117].

BlueTec, GmbH, Germany has developed a new generation absorber (eta plus) for solar hot water applications by sputtering method [118]. The eta plus coating has high absorptance of 0.95 and low thermal emittance of 0.05 at 100°C. The coating performance was evaluated by Fraunhofer Institute for Solar Energy Systems, ISE, Freiburg, Germany. Based on their results, eta plus can be used at collector stagnation temperatures up to 295°C without reducing the collector life [118].

TiN_xO_y coatings with SiO_2 antireflection coating were deposited on Cu and Al substrates by activated reactive evaporation method [119,120]. The coatings deposited on Cu substrate

exhibited absorptance of 0.94 and emittance of 0.04 at 100°C. These coatings were thermally stable in vacuum up to 400°C, whereas the coating degraded when exposed to air [121].

TiNOX energy, a commercial TiN_xO_y cermet on copper substrate is produced by an Italian-German company called Almeco-TiNOX [122,123]. TiNOX, GmbH is currently known as Almeco-TiNOX, GmbH, Germany. Their products are TiNOX energy Al, TiNOX energy Cu and TiNOX artline. TiNOX energy Cu and TiNOX artline have an absorptance of 0.90-0.95 and emittance of 0.04-0.05 at 100°C. The coating has passed the International Energy Agency Task X Service Lifetime and Performance Criterion Tests. Similarly, the Center for Plasma Technologies-PLASMA developed and produced spectrally selective coatings based on Cu and Al absorbers for solar hot water collectors [124]. The coatings are based on titanium composites, i.e., $TiC/TiO_xN_y/AlN$. The coatings exhibited high thermal stability (450°C), corrosion stability and good optical properties ($\alpha = 0.95$; $\varepsilon < 0.10$).

Table 1. Absorptance, emittance and thermal stability of physical vapor deposited mid- temperature solar selective coatings.

Material	**Substrate**	**Deposition Method**	**α**	**$\varepsilon_{100°C}$**	**Stability**		**Refs.**
					Air (°C)	**Vacuum (°C)**	
Black chrome	Cu	Vacuum evaporation	0.80	0.05		200	37-39
Cr_2O_3/Cr with Cr_2O_3 ARC	Ni plated SS	Sputtering	0.92	0.08	300 (64 h)	-	40
Te	Al, Au, Cr, Mo and Cu	Vacuum evaporation	0.90-0.92	0.02-0.05	-	-	66,67
Al-Ge-SiO	Glass	Vacuum evaporation	0.79	0.01	240	-	71
Al-PbS-SiO	Glass	Vacuum evaporation	0.79	0.01	240	-	71
Ni-Ge-SiO	Glass	Vacuum evaporation	0.85	0.03	240	-	71
Ni-PbS-SiO	Glass	Vacuum evaporation	0.92	0.04	240	-	71
Cr-Ge-SiO	Glass	Vacuum evaporation	0.90	0.11	240	-	71
Cr-PbS-SiO	Glass	Vacuum evaporation	0.94	0.12	240	-	71
PbS with ZrO_2 ARC	Al coated glass	Sputtering	0.80	0.02	-	-	72
Co-Al_2O_3 with Al_2O_3 ARC	Ni	Vacuum evaporation	0.95	0.07	-	-	74
Co-Al_2O_3 with Al_2O_3 ARC (Double layer cermet)	Mo	Vacuum evaporation	0.90	0.02 at 50°C	-	-	75

Cu-SiO_2 with SiO_2 ARC (Double layer cermet)	Cu	Vacuum evaporation	0.92	0.02 at 50°C	-	-	75
Ag-Al_2O_3	Cu coated Glass	Vacuum evaporation	0.90	0.03		400 for 100 h	76
Cu-spinel	Cu coated Glass	Vacuum evaporation	0.87	0.06		300 for 100 h	76
Cu_2O/MgF_2	SS	Sputtering+ thermal oxidation	0.80	-	-	-	81
Cr-Cr_2O_3	Cu	Sputtering	0.90-0.94	0.04	-	-	82
Cr_xO_y-Cr-Cr_2O_3	Cu	Sputtering	0.89-0.91	0.05-0.06	275 (50 h)	500 (2 h)	83
Cr-Cr_2O_3	Cu	Sputtering	0.92-0.96	0.05-0.08	-	300-400(1 h)	84
Cu-Al_2O_3	Cu	Sputtering	0.86-0.90	0.03 at R.T.		<300	87
Fe-SiO_2	Cu coated glass	Sputtering	0.91	0.03 at R.T	-	400 (100 h)	87
Metal carbides	Bulk Cu	Sputtering	0.76-0.80	0.02-0.03	-	400 (120 h)	89
Metal silicides	Bulk Cu	Sputtering	0.75-0.81	0.02-0.03	-	400 (100-400 h)[a]	90
Ni-C	Cu, Ni	Sputtering	0.80-0.90	0.02-0.04 at 150°C	-	400 (6 h)	91
SS-C (graded)	Cu coated glass	Sputtering	0.94	0.03	-	300	92
Cu-C	Glass	Sputtering	0.94	0.04 at 120°C	-	500 (1 h)	93
Cu-SS-a-C	Glass	Sputtering	>0.90	<0.05 at 300°C	-	400 (4 h)	101
Al/Al-C-F with Al-C-F ARC	Glass	Sputtering	0.93-0.97	0.07-0.08 at R.T.	-	-	104
Al/Al-C-O with Al-C-F ARC	Glass		0.93	0.06 at R.T.	-	-	

Al/AlN	Glass		0.93	0.04 at R.T.	400	-	107
Cu/SS-C-O/Al-C-F Cu/SS-C/a-C:H	Glass Glass	Sputtering	0.93 0.94	0.03 at R.T. 0.03 at R.T.	- -	- -	104
Cr_2O_3/CrN*	Cu	Sputtering	0.93	0.07	250	-	116
Ge or Si-CaF_2	Quartz	Sputtering	0.70	0.07 at 500°C	-	<500	125
Graphite	Cu, Ni, Ti and Ag	Vacuum evaporation	0.71-0.80	0.01-0.02	-	300	126
Cu-SiO_2/Cu	Glass	Vacuum evaporation	0.93	0.05	-	277	127
TiN_xO_y**	Cu	Sputtering	0.95	0.05	300	-	122 128
$NiCrO_x$	SS	Sputtering	0.80	0.14	-	<200	129, 130
Ti-TiN_xO_y	Cu	Sputtering	0.91	0.04	-	-	131
Ni-NiO***	Al	Sputtering	0.96	0.10	-	300	132
a-C:H/Cr****	Cu	Sputtering	0.92	0.08-0.09	220 (280 h)	-	133
a-C:H/Ti	Al	PVD/ PECVD[#]	0.87	0.06	220 (150 h)	-	134
a-Si:C:H/Ti	Al	PVD/PECVD	0.75		250 (500 h)	-	135

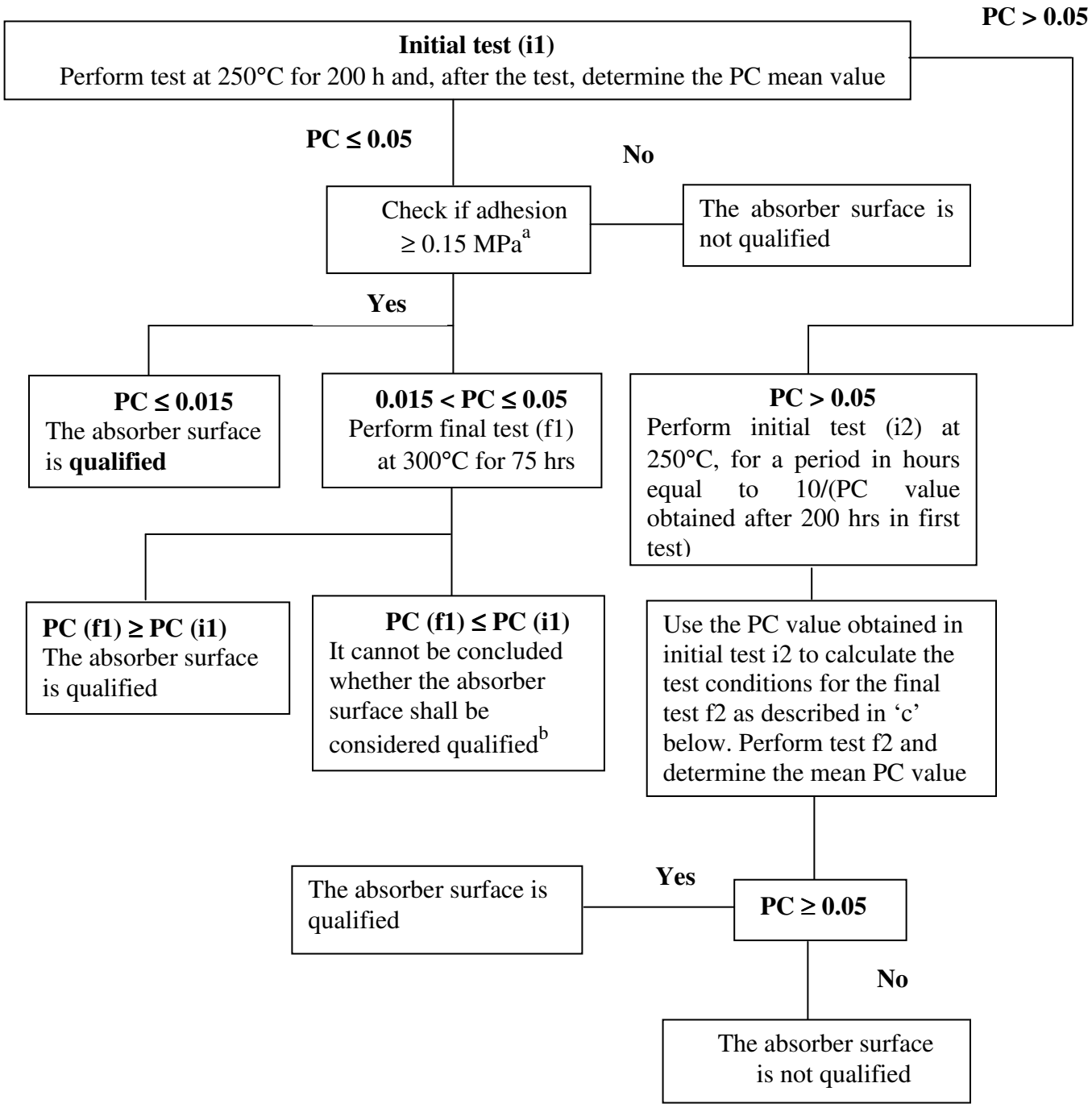
[a]Thermal stability depends on metal layer.

(Marketed by *Alanod® Solar; **Almeco-TiNOX; ***Sunstrip; **** IKARUS Coatings)**,**

[#]Plasma enhanced chemical vapor deposition (PECVD)

Table 2. Testing procedure for qualification of the thermal stability of absorber surfaces

For more details please refer Ref. 111 (Reprinted with permission from Ref. 111).



[a]If a tape test is used to check the adhesion between the coating and the substrate, the adhesion between the tape and the coating should be better than 0.15 MPa.

[b]A more comprehensive investigation of the thermal stability is recommended.

[c]Estimate by interpolation, the testing time, that would correspond to PC = 0.05. Determine the lowest acceptable activation energy on the 250°C curve in Fig. 3 from Ref. 111 and also the corresponding failure time in a test at 200°C and perform the test for a period corresponding to that time. Determine after the test PC and if relevant also the adhesion of the coating.

Table 3. List of commercially available mid- temperature solar selective coatings.

Company	**Coating**	**Absorptance (α)**	**Emittance (ε)**	**Thermal Stability**
Nitto Kohki, Japan	SS-C	0.93	0.04 at 100°C	300°C in vacuum
Alanod Solar, Germany	Sunselect (Cu) (CrN-Cr_xO_y) Mirotherm® (Al) Mirosol® (Al)	0.95 0.95 0.90	0.05 at 100°C 0.05* 0.15*	-
TurboSun, China	W-AlN SS-AlN	0.92-0.94 0.94-0.95	0.08-0.10 at 350°C 0.12-0.14 at 350°C	350-500°C in vacuum
BlueTec, Germany	eta Plus (Cermet coating)	0.95	0.05 at 100°C	295°C
Almeco-TiNOX, Germany	TiNOX energy Al TiNOX energy Cu	0.95 0.95	0.04 at 100°C 0.04 at 100°C	- -
S-Solar (Sunstrip), Sweden	Ni-NiO	0.96	0.10 at 100°C	300°C
PLASMA, Macedonia	TiC/TiO_xN_y/AlN	0.95	<0.10 at 100°C	350°C
IKARUS Coatings, Germany	a-C:H/Cr	0.92	0.08-0.09 at 100°C	250°C
Schott (Spezialglas), Germany	ALUXID®	0.95	0.05*	280°C

*measurement temperature not known

Ni-NiO graded index coatings on aluminum substrates are commercially produced by S-Solar, Sweden (formerly known as Sunstrip, Sweden) [132,136,137]. The S-Solar was established during 2009 through a merger of Sunstrip AB and Exoheat AB. The commercial absorber coating has a solar absorptance in the range of 0.94-0.96 and thermal emittance of 0.13-0.15 at 100°C. The high absorptance can be achieved by decreasing the refractive index from the substrate to the surface. The coating consists of three layers: a nickel barrier layer, a selectively absorbing Ni-NiO layer and an antireflection coating. The coating has passed stability tests according to the procedures recommended by International Energy Agency Task X working group on accelerated life testing of solar energy materials [108-111]. The Swedish Testing and Research Institute has carried out a number of tests on Sunstrip's sputtered absorbers [138]. The tests were conducted in accordance with the requirements and methods stipulated by International Energy Agency, Task X. The tests included checking the durability of the surface against condensation, sulphur oxide and high temperatures. Sunstrip's test results were approved and the values correspond to a product life span of over 25 years [138].

In early 2000, Schuler et al. developed transition metal containing amorphous hydrogenated carbon films (a-C:H/TM, TM = Ti, Cr) or transition metal containing silicon-carbon films (a-Si:C:H/TM) by combined PVD and PECVD process [110,133,134,135]. These coatings can be fabricated by sequential deposition of pure transition metal (Ti, Cr), a-C:H/TM and pure a-C:H. A solar absorptance of 0.87 and emittance of 0.06 at 100°C have been achieved for a-C:H/Ti coatings, whereas, a-C:H/Cr exhibited an absorptance of 0.92 and emittance of 0.08-0.09. The performance criterion evaluation of the a-C:H/Ti coatings during accelerated aging at 220 and 250°C is shown in Figure 7. At a temperature of 250°C, the a-C:H/Ti coatings failed after 55 h. According to the acceptable failure time criteria as discussed previously, the

coating life time should exceed 150 h at 220°C [108]. Therefore, accelerated aging tests indicated that the service life time of the a-C:H/Ti coatings was more than 25 years. Similarly, a-C:H/Cr coating has been reported to pass the accelerated aging tests (Figure 8), which are commercially produced by IKARUS Coatings, Germany [133].

4. Survey of high- temperature solar selective coatings

The efficiency of photothermal conversion at high- temperatures strongly depends on the optical properties and thermal stability of the component materials used in the solar absorbers. For CSP applications, the spectrally selective coatings should have high absorptance (>0.95), low emittance (<0.10) and thermal stability above 400°C in air and vacuum. In addition, long term thermal stability of the coatings in air and vacuum is also an important requirement for high- temperature solar selective coatings. Furthermore, the coatings should have high oxidation resistance and chemical inertness. For high- temperature applications, low emittance is an important parameter, because the thermal radiative losses of the absorbers increase proportionally by T^4 [48]. Several transition metal based cermet coatings have been developed for high- temperature solar thermal applications, because of their refractory nature [48]. The choice of the dielectric material is also very important for the performance of the selective absorber. In general, dielectric materials with low refractive index are preferred in order to reduce the front surface reflections of the cermet coating [48]. Al_2O_3 is widely used as a dielectric material in cermet coatings due to its low refractive index (n = 1.65) and high thermal stability. A large number of cermet coatings have been developed using Pt, Ni, Mo, W as metals and Al_2O_3 as the dielectric material and are discussed below [31,139].

4.1. Evaporation

Evaporation method is the most successful method to develop multilayer absorber coatings on highly reflective substrates. The multilayer coating is designed to produce selective optical interference in the solar region and to be transparent in the infrared region. A well-known example of a multilayer absorber is Al_2O_3-Mo-Al_2O_3, also known as AMA coating, which was developed for high- temperature applications by Schmidt and Park [140]. The AMA multilayer absorber coating has been developed for high- temperature space borne applications [140,141]. A semitransparent Mo layer (20 nm thick) was sandwiched between two Al_2O_3 dielectric layers. The spectral reflectance of the AMA coating deposited on molybdenum substrate is shown in Figure 9. The AMA coating exhibited an absorptance of 0.85 and emittance of 0.22 at 1000°C and 0.11 at 500°C. The coatings deposited on Mo substrate were thermally stable in vacuum at 920°C for 500 h. In order to avoid the usage of costly Mo substrate, the coatings were deposited on Mo coated stainless steel substrates. At temperatures of ~900°C, the AMA coating on Mo-coated SS substrate degraded, whereas the coating on Mo substrates started degrading at 1050°C. Auger electron spectroscopy analysis indicated that the stainless steel samples failed because of the diffusion of Fe and Cr from the stainless steel substrate [141]. The AMA coating had good thermal stability in vacuum, but exhibited limited durability when exposed to air (thermally stable in air at 400°C for 24 h). Based on the AMA design, various other multilayer absorbers using different metals (e.g., Mo, W, Al, Hf, Ni) and dielectric layers (e.g., Al_2O_3, HfO_2, SiO_2, AlN) have been developed for high- temperature applications [30].

Craighead et al. developed Ni-Al_2O_3 and Pt-Al_2O_3 cermet coatings on fused quartz substrates by co-evaporation method [142,143]. The transmission electron micrograph of Ni-Al_2O_3 cermet clearly showed the presence of spherical Ni particles (diameter of 5-10 nm) embedded in aluminum oxide matrix [142]. The electron diffraction studies indicated that the Ni particles were crystalline and aluminum oxide was amorphous in nature. Whereas, for Pt-Al_2O_3, the electron diffraction pattern showed only diffused rings, which is typical of an amorphous solid [143]. The cermet coatings deposited with a graded composition exhibited an absorptance of 0.94 and emittance of 0.10 at 150°C. Ni-Al_2O_3 coatings deposited on Cu substrate were thermally stable in air up to 400°C and the coatings deposited on Ni substrates were stable at 500°C for 100 h. Pt-Al_2O_3 coatings deposited on Pt coated fused quartz substrates exhibited better stability than the Ni-Al_2O_3 coating on Ni coated fused quartz substrates. The Pt-Al_2O_3 coatings showed no degradation in the optical properties even after heating the coatings in air at 600°C for 300 h. A graded index Pt-Al_2O_3 cermet coating overcoated with a microscopically textured SiO_x layer on quartz substrates was also developed by Craighead et al. [144]. The Pt-Al_2O_3 cermet was produced by co-evaporation of Pt and Al_2O_3 from independently controlled electron beam sources. A thin Pt layer (100 nm thick) was deposited on top of a heated quartz substrate. By continuously varying the deposition rates of Pt and Al_2O_3, a graded Pt-Al_2O_3 cermet coating was deposited on top of the Pt layer. The graded cermet was completely metallic near the substrate and completely dielectric on the surface. An absorptance of 0.94 was achieved for the graded Pt-Al_2O_3 cermet coating. The addition of a textured SiO_x antireflection coating on top of the graded Pt-Al_2O_3 cermet increased the absorptance from 0.94 to 0.98, which is shown in Figure 10 [144]. They have also developed various other cermets such as V/Al_2O_3, Fe/Al_2O_3, V/SiO_2, V/MgO and Fe/MgO by co-evaporation method [145]. The authors found that these

coatings were not as suitable as Ni/Al_2O_3 cermets for solar energy applications. Tables 4-7 show the absorptance, emittance and thermal stability of various physical vapor deposited high-temperature solar selective coatings.

Like Ni-Al_2O_3 and Pt-Al_2O_3 cermets, Nyberg and Buhrman also developed Mo-Al_2O_3 cermets using two different designs: 1) standard graded-index tandem absorber and 2) modified design, which are shown in Figure 11 [146]. In the standard design, a graded Mo-Al_2O_3 cermet was deposited on top of a Mo reflector and overcoated with an aluminum oxide antireflection coating. This coating exhibited an absorptance of 0.92 and emittance of 0.07 at 200°C. The deposition temperature was 400°C for the standard design. When the deposition temperature was increased to 600°C, Mo-Al_2O_3 cermets with the standard design exhibited higher absorptance ($\alpha = 0.975$), emittance ($\varepsilon_{200°C} = 0.08$) and surface roughness than coatings deposited at 400°C. In the modified design, the bottom composite layer acts as a roughening template in order to create absorber layers with higher roughness (see Figure 11(b)). The modified Mo-Al_2O_3 cermets exhibited very high absorptance of 0.99 without introduction of any new process steps [146]. On the other hand, Craighead et al. used reactive ion etching method to roughen the SiO_x antireflection coating in order to reduce the front surface reflection resulting in an absorptance of 0.98 for Pt-Al_2O_3 cermet, as discussed previously [144]. Zhang et al. used the double layer cermet concept to develop Mo-Al_2O_3 coatings on Mo and Cu substrates [147]. An absorptance of 0.95 and an emittance of 0.08 at 350°C were achieved for these coatings.

Table 4. High- temperature solar selective coatings – Single layer cermets

Material	**Substrate**	**Deposition Method**	**α**	**ε**	**Stability**		**Refs.**
					Air (°C)	**Vacuum (°C)**	
Single Layer Cermets							
Au-MgO	Mo coated SS	Sputtering	0.90	0.10 at 100°C	400 (64 h)		76, 148, 149,150
Cr-Al_2O_3	Cu coated Glass	Vacuum evaporation	0.92	0.03 at R.T.		500 for 100 h	76
Ni-Ni-SiO_2-SiO_2	Quartz, SS	Vacuum evaporation	0.90	0.07 at 300°C	-	420 (40 h) 515 (12 h)	151
Ni-Ni-MgO-SiO_2	Quartz, SS	Vacuum evaporation	0.88	0.05 at 300°C	-	420 (40 h) 515 (12 h)	151
Ni-MgF_2	Ni	Sputtering	0.96	0.13 at 100°C	450 (446 h)	-	152
Pt-Al_2O_3 with Al_2O_3 ARC	Pt, Cr, Mo coated glass	Sputtering	0.89-0.91	0.13-0.14 at 20°C	400-600 (100 h)	-	153,154 ,155
Pt-Al_2O_3 with Al_2O_3 ARC	Mo or W coated SS	Sputtering	0.92	0.14 at 300°C	400 (H_2) (50-60 h)	-	156
	Mo or W coated superalloy	Sputtering	0.92	0.14 at 300°C	600 (H_2) (36-50 h)	-	156
Fe-Al_2O_3 with Al_2O_3 ARC	SS Superalloy	Sputtering	0.95	0.14 at 427°C	400-500 (36 h) ($Ar+H_2$) 600 ($Ar+H_2$)	-	157
Ni-Al_2O_3 with SiO_2 ARC	Mo-Ni-SS	Sputtering	0.94	0.07 at 100°C	500 (1000 h)	-	158

Cr-SiO	Cu, Cr/Cu	Sputtering	0.80-0.96	0.02-0.12 at 100°C	400-600 (Ar) 450 (28 days)	400-600 (28 days)	159,160
Ti:Al_2O_3	Al	Pulsed laser deposition	0.86	0.01 at R.T.	-	-	161

Table 5. High- temperature solar selective coatings – Double layer cermets.

Material	**Substrate**	**Deposition Method**	**α**	**ε**	**Stability**		**Refs.**
					Air (°C)	**Vacuum (°C)**	
SS-AlN with AlN ARC	Al coated glass	Sputtering	0.94-0.95	0.12-0.14 at 350°C	-	330-400	113,114
Mo-Al_2O_3 with Al_2O_3 ARC	Cu	Vacuum evaporation	0.95	0.08 at 350°C	-	-	147
Mo-Al_2O_3	-	Sputtering	0.94	0.05 at R.T.	-	-	162
Ni-SiO_2	Al and Cu	Sputtering	0.90-0.96	0.03-0.14 at R.T.	-	-	163
Mo-SiO_2	Quartz	Sputtering	0.95	0.097 at 80°C	-	800 (2 h)	164
W-AlN with AlN ARC	Al coated Cu	Sputtering	0.92-0.94	0.08-0.10 at 350°C	-	500 (1 h)	165
Mo-AlN with AlN ARC	Cu	Sputtering	0.92-0.94	0.08-0.10 at 350°C	-	350-500	166
Mo-SiO_2	SS	Sputtering	0.94	0.13 at 580°C	-	580 (6 h)	167

Table 6. High- temperature solar selective coatings – Multilayers/graded cermets.

Material	Substrate	Deposition Method	α	ε	Stability		Refs.
					Air (°C)	Vacuum (°C)	
Al_2O_3-Mo-Al_2O_3	Molybdenum	Vacuum evaporation	0.85	0.11 at 500°C	400	920 (500 h)	140,141
Ni/Ni-Al_2O_3	Cu Quartz	Vacuum evaporation	0.94 0.96	0.22 at 150°C 0.22 at 150°C	300 500 (100 h)	-	142,143, 145
Pt/Pt-Al_2O_3	Cu Quartz	Vacuum evaporation	0.94 0.94	0.19 at 150°C 0.19 at 150°C	400 600 (300 h)	-	143
Al_2O_3-(Pt-Al_2O_3)-Al_2O_3	Pt, Cr, Mo coated glass	Sputtering	0.89-0.91	0.13 at 20°C	450-500 (100 h)	-	153
Pt-Al_2O_3 multilayers	Quartz,	Sputtering	0.95	0.08-0.20 at 827°C	700 (300 h)	-	168
Al_2O_3/M/Al_2O_3 (M-Ni, Cr, Ta, Pt and Mo)	Glass	Sputtering	0.89-0.95	0.14-0.25 at 537°C	300-600* (100-150 h)	400-700*	155
Mo-Al_2O_3	SS	Sputtering	0.91-0.93	0.19-0.27 at 80°C	-	500 (2 h)	169
Al_xO_y-Al-Al_xO_y	Cu Mo	Sputtering	0.95-0.97 0.93-0.95	0.05-0.08 at 82°C 0.05-0.09 at 82°C	400 (2 h) 400 (2 h)	- 800 (2 h)	170
Al_2O_3/Cu/Al_2O_3/AlCuFe homogeneous/Al_2O_3	Cu coated Si wafer	Sputtering	0.89-0.90	0.04-0.06 at 400°C	400 (450 h)	-	171
Al_xO_y-AlN_x-Al	Quartz glass	Sputtering	0.94-0.97	0.07 at 82°C	-	400-600 (30 min)	172

$Mo/HfO_x/Mo/HfO_2$	Cu	Sputtering	0.90-0.92	0.07-0.09 at 82°C	400 (2 h)	600 (2 h)	173
NREL #6A	SS	Sputtering	0.95	0.08 at 500°C	500	-	174,175
NREL #6B	SS	Sputtering	0.95	0.10 at 500°C	500	-	174,175
$W/W\text{-}Al_2O_3/Al_2O_3$	SS	Sputtering	0.93	0.10 at 400°C 0.14 at 550°C	-	580 (30 days)	176

*Thermal stability depends on metal (M) layer and Al_2O_3 deposition conditions

Table 7. High- temperature solar selective coatings – Single layers/Tandem absorbers.

Material	Substrate	Deposition Method	α	ε	Stability		Refs.
					Air (°C)	Vacuum (°C)	
TiN_x	Ag coated glass and SS	Sputtering	0.86-0.88	0.024-0.033 at 127°C	-	600 (500 h)	177
ZrN_x	Ag coated glass and SS	Sputtering	0.86-0.88	0.024-0.033 at 127°C	-	600 (500 h)	177
ZrC_xN_y	Ag coated glass and SS	Sputtering	0.86-0.88	0.024-0.033 at 127°C	-	600 (500 h)	177
ZrO_xN_y	Ag coated glass and SS	Sputtering	0.88-0.93	0.08-0.30 at 327°C	-	600 (500 h)	177
TiAlN/TiAlON/Si_3N_4	Cu SS	Sputtering	0.93-0.94 0.93-0.95	0.05-0.08 at 82°C 0.15-0.17 at 82°C	550 550	600 -	178,179 ,180,
TiAlN/AlON	Cu	Sputtering	0.93-0.94	0.05-0.06 at 82°C	550 (2 h)	800 (2 h)	181
NbAlN/NbAlON/Si_3N_4	Cu	Sputtering	0.93-0.95	0.07 at 82°C	500 (2 h)	600 (2 h)	182
TiAlN/CrAlON/Si_3N_4	Cu	Sputtering	0.94-0.95	0.05-0.07 at 82°C	500 (2 h)	800 (2 h)	183
TiAl/TiAlN/TiAlON/ TiAlO	SS, Cu	Sputtering	0.90	0.09-0.19*	650 (1 h)	-	184
Ti_xAl_{1-x}/TiN/$(TiN\text{-}AlN)_H$/ $(TiN\text{-}AlN)_L$/AlN	Polished SS	Sputtering	0.94	0.08 at 82°C	400 (2 h)	-	185
$Ti_{0.5}Al_{0.5}N/Ti_{0.25}Al_{0.75}N$/AlN	SS	Sputtering	0.94	0.04 at 82°C	-	-	186

*measurement temperature not known

Graded Ni-MgO, Ni-SiO_2 and Ni-MgF_2 cermet coatings were also studied for high-temperature applications [151,152]. Okuyama et al. developed Ni-MgO and Ni-SiO_2 cermets with SiO_2 antireflection coating [151]. The coatings were deposited on quartz plates for optical measurements and on stainless steel substrates for emittance measurements. Absorptance values of 0.90 and 0.88 were achieved for Ni-SiO_2 and Ni-MgO cermets, respectively. The reflectance spectra of these coatings at different operating temperatures are shown in Figure 12. Both the coatings were thermally stable in vacuum at 420°C for 40 h and at 515°C for 12 h. Ni-MgF_2 cermets deposited on Ni substrates exhibited an absorptance of 0.96 and emittance of 0.13 at 100°C. No significant degradation in the optical properties was observed even after the coatings were heated in air at 450°C for 446 h [152].

A large number of high- temperature solar selective coatings were developed by the evaporation method. However, this method cannot be used to deposit coatings on large areas or complex shaped substrates such as long tubes, which are required for solar thermal power generation applications. Sputtering method, by contrast, has been widely used to deposit solar selective coatings uniformly on large area substrates.

4.2. Pulsed laser deposition

Pulsed laser deposition (PLD) is a very simple thin film deposition method which has been successfully used to deposit a wide range of materials such as high- temperature superconducting thin films, optical coatings, magneto-resistive thin films, etc. [187-190]. But the major disadvantages of PLD method are that it often produces particulates ranging in size from 10 nm to few μm in diameter, which can contaminate the growing film and deposition on large area samples with uniformity is very difficult [187]. Because of these reasons, this method has not been used widely to deposit solar selective coatings. Even though PLD has been used

widely to deposit optical thin films, there are only a few reports wherein PLD has been used to deposit cermet based solar absorber coatings [161]. For example, Chen et al. have studied the optical properties of Ti:Al_2O_3 thin films deposited using PLD method and have reported a very low reflectance in the visible region and very high reflectance in the infrared region [161].

4.3. Ion plating

Lei et al. developed spectrally selective TiAl/TiAlN/TiAlON/TiAlO coating on SS and Cu substrates by multi-arc ion plating system [184]. The coatings exhibited high absorptance of 0.90 and emittance of 0.08-0.19 and the coatings were thermally stable in air up to 650°C for 1 h. They also developed TiAl/TiN/$(TiN\text{-}AlN)_H$/$(TiN\text{-}AlN)_L$/AlN on polished SS substrates by magnetron sputtering technique. The coatings were thermally stable in air at 500°C for 2 h with a solar selectivity of 0.94/0.08 [185,191].

4.4. Sputtering

Various researchers have developed Pt-Al_2O_3 cermet coatings by magnetron sputtering method [153,154,156,168,192]. Thornton and Lamb investigated three coating configurations of Pt-Al_2O_3 cermets: (1) Pt-Al_2O_3 cermet with a linearly graded platinum content and an Al_2O_3 antireflection coating, deposited on platinum coated glass, (2) Pt-Al_2O_3 coating with a uniform platinum content and an Al_2O_3 antireflection coating, prepared on Pt, Cr and Mo coated glass and (3) Al_2O_3/Pt-Al_2O_3/Al_2O_3 coating deposited on Pt, Cr and Mo coated glass [153,154,192]. The coatings were deposited using two cylindrical-post magnetron sputtering guns, one of which contains an alumina target and other contains an electroplated platinum target. All the three configurations exhibited absorptance greater than 0.90. For the graded and AMA configurations, emittance less than 0.10 was obtained, whereas, for the uniform cermet the emittance was 0.13 at room temperature. Graded, uniform and AMA coatings deposited on platinum coated glass

substrates were stable in air at 600°C for 100 h. Whereas, coatings deposited on Cr or Mo coated glass substrates were less stable, however, they showed promise for many applications in the temperature range of 300-500°C [153]. Thornton and Lamb also investigated the thermal stability of Al_2O_3/M/Al_2O_3/R coatings with M layers of Mo, Cr, Ni, Ta and Pt-Al_2O_3 cermet and R layers of the same metal as the M layers, except for Pt-Al_2O_3, where they were chromium or molybdenum [155]. They used glass plates as substrates and the coatings were deposited using planar magnetron sputtering sources. The Al_2O_3 layers were deposited by both direct RF sputtering of alumina and also by the reactive sputtering of aluminum targets. The thermal stability of this multilayer absorber coating mainly depends on the method of preparation of the Al_2O_3 layer. The multilayer absorber coatings were heat-treated in air and vacuum over the temperature range of 300-700°C for periods from 8 to about 1000 h. The Al_2O_3/M/Al_2O_3/R coatings with reactively sputtered Al_2O_3 layers and M layers of Cr and Ta were stable up to 300°C and those with Ni, Mo or Pt-Al_2O_3 layers were stable in air/vacuum at 400-450°C. Whereas, Al_2O_3 layers deposited by RF sputtering of alumina with M layers of Cr, Ni or Pt-Al_2O_3 layers were stable up to 500-600°C in air and 650-700°C in vacuum [155]. Similarly, detailed studies on graded Pt-Al_2O_3 cermet coatings on glass substrates with Pt interlayer have been reported by Thornton and Lamb [154]. The heating of this coating in air up to 600°C, indicated an increase in emittance to approximately 0.25 from approximately 0.05 for reactively sputtered Al_2O_3 based coatings. The emittances of these coatings were measured at 20°C. However, the RF sputtered Al_2O_3 based cermet coating showed less emittance when compared to reactively sputtered Al_2O_3 based coatings (Figure 13).

Vien et al. prepared Pt-Al_2O_3 cermet coatings on SS and superalloy substrates by RF co-sputtering [156]. The coatings exhibited an absorptance of 0.92 and an emittance of 0.14 at 300°C. The coatings deposited on SS and superalloy substrates were thermally stable at 400 and 600°C in hydrogen atmosphere, respectively. Pt-Al_2O_3 and Al_2O_3/$MoSi_2$ multilayer cermet coatings were prepared by RF magnetron sputtering for high- temperature solar applications. These coatings were optimized by computer simulations [168]. The tetragonal-$MoSi_2$/Al_2O_3 multilayers have solar absorptance up to 0.92 and emittance of 0.15 (1100 K). A high solar absorptance of 0.95 and emittance of 0.10 have been achieved for Pt-Al_2O_3 multilayers [168]. These coatings were thermally stable in air at 600°C for 400 h. It is clearly evident from the above mentioned results that the Pt-Al_2O_3 coatings are promising candidates for high-temperature solar thermal applications. But the coatings are not commercialized due to the high cost of platinum. Ni-Al_2O_3 cermet coating is an alternative for Pt-Al_2O_3 cermets in terms of cost and high- temperature optical performance. These coatings were initially developed by evaporation and anodization methods [142,143,193]. The anodized Ni-Al_2O_3 cermet coatings have poor thermal stability at elevated temperatures. It is well known that the optical properties of thin films depend on their method of preparation. The coatings prepared by chemical conversion, electrodeposition and vapor deposition methods fail at higher operating temperatures because of compositional instabilities and also because of poor adhesion [194]. On the other hand, sputtered coatings are found to have uniform composition and excellent adhesion to the substrate. Ni-Al_2O_3 coatings were prepared on different substrates such as Ni plated SS, Mo coated SS, Cu coated SS and Mo coated nickel plated SS by RF sputtering method. The graded Ni-Al_2O_3 cermet coatings (65 nm thick) with 78 nm thick SiO_2 antireflection coating deposited on molybdenum or nickel plated stainless steel substrates resulted in an absorptance of 0.94 and

an emittance of 0.07 at 100°C [158]. The Ni-Al_2O_3 cermet coatings with SiO_2 antireflection coating deposited on Mo coated Ni plated SS substrates were thermally stable in air at 500°C for 1000 h. Whereas, coatings without SiO_2 antireflection coating were stable in air only up to 400°C [158]. Sella et al. also developed a low cost Fe-Al_2O_3 cermet with an Al_2O_3 antireflection coating for high- temperature solar thermal applications [157]. The coatings were deposited on SS substrates covered with or without tungsten or molybdenum. This three layer stack (Mo/Fe-Al_2O_3/Al_2O_3) exhibited high absorptance of 0.95 and low emittance of 0.06 at room temperature. The coating deposited on stainless steel substrate without Mo interlayer was stable up to 400-500°C, while the coating deposited on superalloy substrates (Nicral, IN 100) was stable up to 600°C in Ar+H_2 atmosphere [157]. Even though the cost of Fe-Al_2O_3 coating is very low, the thermal stability of the coating is poor when compared to the Pt-Al_2O_3 coatings.

Various researchers have prepared Mo-Al_2O_3 cermet coatings for high- temperature solar applications [82,162,169]. Mo-Al_2O_3 cermet coated tubes have been used in the solar thermal power plants which will be discussed in section 4.5. Recently, Xinkang et al. prepared a series of Mo-Al_2O_3 cermet coatings by DC and RF magnetron sputtering methods [169]. The optimized coating deposited on SS substrate has four layers, i.e., Mo/Mo-Al_2O_3-HMVF/Mo-Al_2O_3-LMVF/Al_2O_3 from bottom to top. This optimized coating exhibited an absorptance of 0.92 and emittance of 0.19 at room temperature. The coatings were thermally stable at 500°C for 2 h in vacuum [169].

In most of the sputter-deposited M-Al_2O_3 based coatings (M: Pt, Ni and Mo), RF and reactive DC sputtering methods have been used [155,158,192]. DC sputtering has serious limitations for the sputtering of oxides and RF sputtering suffers from low growth rates and its

complexity. Pulsed sputtering has been developed for the deposition of highly adherent, uniform and dense coatings of dielectric nitrides and oxides with high growth rates [195]. Recently, our group developed spectrally selective $Al_xO_y/Al/Al_xO_y$ multilayer absorber coatings on copper and molybdenum substrates using a pulsed sputtering system [170]. Asymmetric bipolar-pulsed DC generators were used to deposit the $Al_xO_y/Al/Al_xO_y$ multilayer absorber coating. The compositions and thicknesses of the individual component layers were optimized to achieve high solar absorptance (α = 0.95–0.97) and low thermal emittance ($\varepsilon_{82°C}$ = 0.05–0.08). The multilayer absorber deposited on Cu substrates exhibited high solar selectivity of 0.90/0.06 even after heat-treatment in air up to 400°C for 2 h. At 450°C, the solar selectivity decreased significantly on Cu substrates (e.g., α/ε = 0.79/0.07). The coatings deposited on Mo substrates were thermally stable up to 800°C in vacuum for 2 h with a solar selectivity of 0.93/0.05.

Eisenhammer et al. developed Al_2O_3 based quasicrystalline cermets for high- temperature solar applications [171]. Generally, the quasicrystals exhibit good oxidation and diffusion stability [196]. Solar selective absorbers based on AlCuFe thin films (i.e., $Al_2O_3/Cu/Al_2O_3/AlCuFe$ homogeneous$/Al_2O_3$) and a cermet of AlCuFe particles embedded in an Al_2O_3 matrix ($Al_2O_3/Cu/Al_2O_3/AlCuFe$ cermet$/Al_2O_3$) were deposited on Cu coated Si wafers by sputtering method [171]. The absorptance of the homogeneous films was found to be 0.89-0.90 and the emittance was 0.04-0.06 at 400°C. Whereas, for the cermet layer, the absorptance and emittance were 0.79 and 0.03, respectively at 400°C. The coatings were thermally stable in air at 400°C for 100 h.

Apart from Al_2O_3, other dielectric materials such as AlN, MgO and SiO_2 are also used in cermet coatings. Fan and Zavaracky used MgO as a dielectric medium and developed Au-MgO

cermets by RF sputtering method. They prepared Au-MgO coatings on copper, aluminum, SS and SS substrate coated with molybdenum using a hot-pressed target with 75 vol% MgO and 25 vol% Au [150]. The coatings deposited on various substrates exhibited absorptance in the range of 0.90-0.93. However, the emittance was 0.04 and 0.10 at 100°C for coatings deposited on Cu and SS substrates, respectively. The coatings were thermally stable in air at 200°C for Cu substrate, 300°C for SS and Al substrates and 400°C for Mo coated stainless steel substrate [150]. Figure 14 shows the reflectance of as-deposited and heat-treated Au-MgO cermets on Mo coated stainless steel substrates. Yue et al. used both aluminum oxide and aluminum nitride dielectric materials to develop an Al_xO_y-AlN_x-Al tandem absorber for high- temperature applications. The coating deposited on quartz substrates exhibited absorptance of 0.88-0.97 and emittance of 0.07-0.10 at 82°C. The coatings were thermally stable at 400-600°C in vacuum. Even after heating the coating at 550°C for 40 h, the absorptance was 0.98 and the emittance was 0.12 [172]. Pekruhn et al. used SiO as a dielectric material and developed Cr-SiO cermets on Cu and Cr/Cu substrates by RF sputtering method [159]. The coatings exhibited absorptance in the range of 0.85-0.95 and emittance in the range of 0.03-0.08 (380 K). The thermal stability of the coatings was studied in the temperature range of 300-900°C in air, vacuum and Ar atmosphere. The coatings were thermally stable in air, argon and vacuum at 600°C for 28 days [160]. Graded Fe-SiO_2 cermets were deposited on Cu coated glass substrates by dual cathode DC magnetron sputtering method. The coating showed absorptance in the range of 0.89-0.91 and emittance of 0.04 at room temperature, and was stable in vacuum at 400°C for 100 h [87]. Farooq et al. prepared a graded index Ni-SiO_2 cermet coating on Al and Cu substrates by co-sputtering method [163]. The coatings were graded from 90% metal volume fraction at the substrate-

coating interface to 10% at the coating-air interface. Solar absorptance of 0.90-0.96 and emittance of 0.03-0.14 at room temperature were achieved for Ni-SiO_2 coatings with SiO_2 antireflection coating [163]. The antireflection coating minimizes the optical interference effects within the film and increases the solar absorptance by 4% (from 0.92 to 0.96). They also prepared various multilayer metal-dielectric graded index solar selective coatings in which the metal volume fraction increases with depth from top to bottom (film-substrate interface) [197-199]. The optimization studies were done on four layer cermets such as V-Al_2O_3, W-Al_2O_3, Cr-Al_2O_3, Co-Al_2O_3, V-SiO_2, Ni-SiO_2, W-SiO_2 and Cr-SiO_2, where the metal volume fractions vary from 0.6 to 0.8. Recently, Wang et al. deposited double layer Mo-SiO_2 coatings with SiO_2 antireflection layer on quartz substrates by sputtering method. The optimized coating exhibited an absorptance of 0.95 and emittance of 0.097 at 80°C with thermal stability at 800°C for 2 h in vacuum [164].

Various transition metal based cermet coatings such as Pt-Al_2O_3, Ni-Al_2O_3, Mo-Al_2O_3, W-Al_2O_3, Mo-SiO_2, Ni-SiO_2, etc., developed for high- temperature applications, were discussed above. These coatings exhibited excellent solar selectivity and thermal stability in vacuum. Whereas, coatings heat-treated in air at high- temperatures (>400°C) started degrading mainly due to oxidation or diffusion of the metal component or both oxidation and diffusion in the cermet coating. In recent years, transition metal nitride and oxynitride coatings have attracted considerable research interest due to their exotic mechanical, chemical, electrical and optical properties. The optical properties of transition metal based nitride/oxynitride/oxide coatings can be tailored by controlling the stoichiometry, which affects the density of free electrons in the transition metal 'd' band [200,201]. Incorporation of an additional element (such as Al) in the transition metal nitride matrix changes the bonding structure (e.g., metallic to covalent). For

example, it is known that transition metal nitrides such as TiN, NbN, CrN, etc. exhibit metallic character and AlN exhibits covalent character [202]. The change in the bonding structure results in variations in the electrical resistivity and the optical properties of transition metal nitride based coatings. Transition metal-based nitride, carbonitride and oxynitride coatings such as TiN, ZrC_xN_y, TiAlN, TiAlON, ZrO_xN_y and TiN_xO_y exhibit good optical properties [119,177,200, 203-205]. Blickensderfer et al. developed few tandem absorbers which comprised of a stainless substrate with a slightly oxidized surface, a thin sputtered coating of reflective silver and a selective absorber coating of substoichiometric zirconium or titanium nitrides, carbonitrides, oxynitride and oxycarbonitrides [177]. TiN_x, ZrN_x and ZrC_xN_y coatings have the best combination of good absorptance and low emittance. ZrO_xN_y coatings exhibited high solar absorptance of 0.93 and high emittance of 0.19 at 127°C [177]. Heat-treatment of these coatings in air at 127°C for 300 h resulted in a decrease in the solar absorptance. Whereas, the coatings exhibited excellent thermal stability in vacuum at 700°C for 500 h [177]. Schüler et al. reported that single layer TiAlN coating shows an absorptance of 0.80 and it can be used as a solar control window coating [200]. According to Luthier and Levy, TiAlON films displayed a low reflectance (below 16%) and high absorption coefficient ($1\text{-}4\times10^5$ cm^{-1}) in the visible-near ultraviolet spectral range [205].

Recently, our group has developed a new generation high- temperature tandem absorber of TiAlN/TiAlON/Si_3N_4 using reactive DC magnetron sputtering [178,179,180]. In this tandem absorber, TiAlN which is metallic in nature acts as the main absorber layer and TiAlON which has low metallic content acts as another absorber layer. The TiAlN/TiAlON tandem absorber exhibited absorptance of 0.90 and emittance of 0.05 at 82°C (on Cu). The solar selectivity of the tandem absorber was increased by 0.95/0.06 by depositing a suitable antireflection coating of

Si_3N_4. The TiAlN, TiAlON layers were nanocrystalline in nature, whereas Si_3N_4 was amorphous as shown in TEM data presented in Figure 15. This tandem absorber is designed in such a way that the refractive indices of three layers increase from surface of the coating to the substrate, which was confirmed by the ellipsometric measurements (Figure 16). The *n* and *k* results clearly showed that the reflectance of the tandem absorber is reduced by gradually increasing the refractive index from surface to the substrate, consequently increasing the absorption [206]. The TiAlN/TiAlON/Si_3N_4 tandem absorber on Cu substrate was found to be thermally stable in air up to 550°C (2 h) and up to 800°C (2 h). The higher thermal stability of the tandem absorber has been attributed to the fact that TiAlN acts as a diffusion barrier layer on Cu substrate and also the constituent layers are thermally stable at higher temperatures [178, 179]. This coating concept has been granted a US patent (Patent No: 07585568) [207]. Based upon the successful demonstration of this coating concept, other tandem absorbers such as TiAlN/AlON, NbAlN/NbAlON/Si_3N_4 and TiAlN/CrAlON/Si_3N_4 have been developed by our group for high-temperature solar selective applications [181-183]. Our initial results on HfMoN/HfON/Al_2O_3 tandem absorbers demonstrated that these coatings exhibit solar selectivity of 0.95/0.13 on SS substrates and are found to be stable up to 600°C for 450 h and 650°C for 125 h in vacuum [208].

Similar to transition metal nitrides, transition metal oxide coatings (such as Cr_2O_3, MoO_3, WO_x, etc.) also have been used for solar selective applications due to their excellent optical properties and good thermal stability [48]. HfO_2 coatings exhibit good mechanical, chemical and thermal stability as well as relatively high dielectric constant and high refractive index [209,210]. A large band gap (5.5 eV) and high refractive index makes HfO_2, an interesting candidate for optical applications. For example, HfO_2 is used as an optical coating for astronomically charged

coupled devices [211], antireflective multilayer coating for night vision devices [212], high reflectivity mirrors and for IR optical devices [213,214]. The optical properties of single layer hafnium oxide thin films have been studied widely [215-218]. Amorphous HfO_2 thin films have been reported to exhibit high transmittivity (80-97%) and low reflectivity (< 15%) in the visible and near IR regions, respectively [215]. HfO_2 based heat mirror (HfO_2/Ag/HfO_2) with an average transmittance of 72.4% in the wavelength range of 700-2000 nm was developed by Al-Kuhaili [210].

Recently, our group has investigated the possibility of designing a dielectric/metal/dielectric multilayer absorber coating of HfO_2 and molybdenum. Solar selective coatings of HfO_x/Mo/HfO_2 were deposited using a pulsed sputtering system [173]. The optimized HfO_x/Mo/HfO_2 multilayer absorber on Cu substrate exhibited high solar absorptance (α = 0.90–0.92) and low thermal emittance ($\varepsilon_{82°C}$ = 0.07–0.09). Similarly, on SS substrates the optimized coatings exhibited absorptance and emittance in the range of 0.90–0.92 and 0.15–0.17, respectively. The HfO_x/Mo/HfO_2 coatings deposited on Cu substrates were thermally stable up to 400°C for 2 h in air. Above 400°C, the absorptance value decreased drastically due to diffusion of Cu from the substrate and its subsequent oxide formation [173]. Addition of a thin Mo interlayer (40 nm) in the HfO_x/Mo/HfO_2 coating (i.e., Mo/HfO_x/Mo/HfO_2) deposited on Cu substrates increased the thermal stability of the coating up to 500°C for 2 h. At temperatures greater than 500ºC, the coating started degrading due to the formation of MoO_2 (Raman bands at 442 and 728 cm^{-1}), and $HfMo_2O_8$ (Raman bands at 87 and 878 cm^{-1}) phases, which was confirmed by micro-Raman spectroscopy studies and is shown in Figure 17. The Mo/HfO_x/Mo/HfO_2 coatings deposited on SS substrates showed no significant changes in

absorptance and emittance values after annealing at 500°C in air and at 800°C in vacuum for 2 h [173].

Similar to HfO_2, ZrO_2 exhibits interesting properties such as high melting point, high strength, toughness and chemical inertness. It has been widely used in various applications such as cutting tools, thermal barrier coatings, solid oxide fuel cells, etc. [202]. Zhang et al. developed Zr-ZrO_2 cermet coatings on Al or Zr substrates by magnetron sputtering method [219]. A physical numerical model has been developed to optimize Zr-ZrO_2 cermet coatings with maximum photo-thermal conversion. The modeling results showed that the cermet coatings deposited on Al reflector with Al_2O_3 antireflection layer have much better solar performance than those on the Zr reflector. A theoretically optimized three layer film consisting of an Al_2O_3 antireflection layer and double layer cermet on Al metal reflector exhibited high solar absorptance of 0.97 and low emittance of 0.03 at 80°C. Whereas, absorptance of 0.96 and emittance of 0.05 at 80°C were achieved for two cermet layers prepared by sputtering method [219]. Initial results showed that these coatings were thermally stable at 300-350°C in air.

C.E. Kennedy modeled a solar selective coating with absorptance of 0.96 and emittance of 0.06 at 400°C using a computer aided design software. This coating is composed of multiple cermet layers (i.e., a-TiSi and TiO_2) and multiple antireflection layers (i.e., SiO_2) [174,175]. C.E. Kennedy has also developed another high- temperature solar selective coating with absorptance of 0.95 and emittance of 0.07 at 400°C [175]. The difference between these two coating is the substitution of a-TiSi by Pt [174].

4.5. Commercially available high- temperature solar selective coatings

A large number of solar selective coatings such as Pt-Al_2O_3, Ni-Al_2O_3, Ni-SiO_2, Fe-Al_2O_3, Cr-SiO, Mo-Al_2O_3, Mo-SiO_2, W-Al_2O_3, etc. have been developed for high- temperature solar thermal applications, as discussed above. But only a few of them such as, Mo-SiO_2, W-Al_2O_3, Mo-Al_2O_3 and M-AlN (M: SS, W and Mo) cermets have been successfully commercialized and are being used in evacuated receiver tubes for solar thermal power generation. Table 8 shows the list of commercially available high- temperature solar selective coatings. Mo-Al_2O_3 cermet coatings have been used on receiver tubes due to their excellent thermal stability in vacuum [220]. These receiver tubes were produced by Luz International Ltd., USA and are used in Solar Energy Generating Systems power plants. The Mo-Al_2O_3 cermet coatings were deposited using planar magnetron sputtering technology consisting of seven planar targets (three metallic and four ceramic targets) wherein, the metal targets were DC sputtered and ceramic targets were sputtered using RF power [220]. The coatings exhibited an absorptance of 0.96 and emittance of 0.16 at 350°C with thermal stability of 350-500°C in vacuum. Despite the fact that this coating is highly stable in vacuum, it has limited thermal stability in air (up to 300°C). It has been reported that the Mo-Al_2O_3 coatings are expensive when compared to other DC sputtered SS-C and Al-N solar selective coatings which are also produced on a commercial scale [221]. All of these commercialized coatings have a graded composite absorber. Zhang et al. used the double layer cermet concept to develop the SS-AlN coatings and these coatings are commercially marketed by TurboSun, China which has been discussed earlier. They have also developed W-AlN and Mo-AlN double layer cermet coatings by sputtering method [165,166,222-224]. A solar absorptance of 0.92-0.94 and emittance of 0.08-0.10 at 350°C were achieved for the W-AlN and Mo-AlN cermet coatings. These coatings are thermally stable at

350-500°C in vacuum and are lower in cost than the Siemens CSP Tubes (formerly Solel Tubes) [166]. Solel's Universal Vacuum Air Collector (UVAC2008) receiver tube uses an Al_2O_3 based multilayer cermet, which has an absorptance of 0.97-0.98 and emittance of 0.07-0.10 at 400°C [225].

Table 8. Commercially available high- temperature solar selective coatings.

Company	Coating	Absorptance (α)	Emittance (ε)	Thermal Stability
Angelantoni-ENEA, Italy	Mo-SiO_2 W/W-Al_2O_3/Al_2O_3	0.94 0.93	0.13 (580°C) 0.10 (400°C) 0.14 (550°C)	580°C in vacuum
Siemens (formerly Solel), Germany	Al_2O_3 based cermet Mo-Al_2O_3 W-Al_2O_3	0.96 0.96 0.96	0.10 (400°C) 0.16 (350°C) 0.16 (350°C)	400°C 350-500°C in vacuum 350-500°C in vacuum
SCHOTT, Germany	–	0.95	0.10 (400°C)	500°C in vacuum

In the past, Solel Solar Systems Ltd. was the only manufacturer of commercially available receiver tubes. Recently, Archimede Solar Energy (ASE), Italy and Schott, Germany began producing collector tubes. ASE produces receiver tubes (HEMS08) for Italian National Agency for New Technologies, Energy and the Environment (ENEA) Solar Thermodynamic Project where the thermal exchange fluid is a molten salt entering at 290°C in the solar field and coming out at 550°C [226]. Therefore, the receiver tube and the solar selective coating have to be stable up to 580°C. The HEMS08 receiver tubes are coated with selective coatings of Mo-SiO_2 (or) W-Al_2O_3 [167,176,227]. Solar absorptance greater than 0.94 and emittance lower than 0.13 at 580°C have been reported for Mo-SiO_2 coatings [167]. The reflectance of as-deposited Mo-SiO_2 coating is shown in Figure 18. The structure of this coating is as follows: Mo/Mo-SiO_2(HMVF)/Mo-SiO_2(LMVF)/SiO_2. Similarly, graded W-Al_2O_3 coating exhibit α/ε(550°C) = 0.93/0.14 and this coating was thermally stable at 580°C in vacuum. They have also developed graded TiN-AlN cermet with AlN or Al_2O_3 antireflection coating exhibiting absorptance of 0.95 and emittance of 0.12 at 580°C [228].

The composition of the PTR® 70 receiver tube developed by Schott, Germany is not known, but has been reported to use a new type of anti-reflection coating on the specially designed iron free glass tube which has a high abrasion resistance and at the same time allows the transmission of more than 96% of the sun's radiation [229]. The absorber coating has an absorptance of 0.95 and low emittance (< 0.10) at a temperature of about 350-400°C [229].

The performance criterion evaluation is important to determine the service lifetime of the solar selective coating. As has been discussed in Section 3.4, such standard accelerated aging procedures are well documented for flat-plate collector applications. However, in the case of

receiver tubes, the operating temperature is usually more than 400°C and the thermal radiative losses of the absorber coating are significantly high. In general, the emittance of the coating is measured either at 82°C using standard emissometer or by measuring the reflectance at room temperature using standard spectrophotometer in the infrared region. In order to measure the emittance at higher temperatures, the coating is usually heated at a given temperature and the emittance is measured ex-situ using the emissometer or spectrophotometer. There are some recent reports wherein FTIR with high temperature attachment has been used to measure the emittance at higher temperature. The instrumentation for measuring the in-situ emittance at high temperature is not well developed and the emittance values reported for high temperature coatings are usually measured ex-situ. To our knowledge, there are no standard test procedures for performance criterion evaluation of high- temperature solar selective coatings. However, the round-robin experiments were conducted in 2005 by leading four laboratories (National Renewable Energy Laboratory (NREL), Sandia National Laboratories, AZ Technologies, Surface Optics Corporation) to confirm the high-temperature emittance measurements for commercially available receiver tubes (viz., Luz cermet, UVAC A, UVAC B, NREL 6A). The details of which can be found in references [175,230].

5. Outlook

In order to make the solar thermal energy more affordable, in addition to improvement in the solar thermal power plant design and associated support structure for solar fields, solar absorber coatings with improved optical properties and thermal stability need to be developed. Solar selective coatings based upon highly stable oxide materials such as Y_2O_3, ZrO_2 and HfO_2 need to be explored [173,219]. The nanocermets are likely to be potential candidates for solar energy conversion because they exhibit strong absorption in the visible region, which occurs

because of surface plasmon resonance phenomena, also known as quantum confinement effect [88]. The optical properties of the nanocermets strongly depend on the particle shape, size, concentration of the particle in the matrix, particle distribution and local dielectric environment of the dielectric matrix [231]. Also there is a need to develop nanostructured materials for solar energy conversion as special physical effects related to the nanometer scale due rise to interesting microscopic properties [133]. For mid- temperature applications, it is also important to develop self-cleaning and transparent superhydrophobic coatings on top of solar absorber coatings to improve the overall efficiency and also to protect the coating from humidity, dust and corrosive environments [232]. For applications, wherein unglazed collectors are required, the solar selective coatings need to be protected by a suitable corrosion resistant coating [233]. Therefore, highly transparent coatings which can survive UV irradiation, abrasion and corrosion resistance need to be developed. In order to improve the overall solar selectivity of the receiver tubes, it is essential to develop a suitable antireflection coating on glass substrates. Hybrid coatings consisting of PVD and other processes (e.g., sol-gel, PECVD) need to be developed in order to reduce the cost of solar absorber coating technology [133]. There is also an urgent requirement to develop a universal test procedure for the performance criterion of the high-temperature solar selective coatings and also to develop instrumentation to measure the emittance at very high temperatures. These are required to determine the life time of the high-temperature solar absorber coatings.

For most of the high- temperature applications, stainless steel is used as the substrate material, which has relatively high intrinsic emittance ($\varepsilon_{82^{\circ}C}$ = 0.10-0.12). The solar selective coating deposited on SS substrates therefore exhibits low spectral selectivity, leading to low photothermal conversion efficiency. Researchers, at present use PVD coated metallic interlayers

to decrease the emittance. This works satisfactorily in vacuum and fails when the coating is exposed to air because of thermal oxidation and interdiffusion along the substrate and the absorber coating. Therefore, suitable interlayer materials with improved oxidation and optical properties need to be developed for achieving high solar selectivity and thermal stability of the absorber coating on the SS substrates. Finally, there is a universal requirement for the development of solar selective coatings, which can operate at very high temperatures in air to simplify the solar energy system design and cost of the solar energy. A considerable research needs to be carried out in this direction, because prolonged heating of solar absorber coatings in air at higher temperatures can not only oxidize the coating, but also can induce other microstructural changes such as particle size orientation, metal volume fraction, particle shape, particle distribution, etc. These changes degrade the overall solar selectivity of the spectrally selective coatings [231].

6. Summary and conclusions

Solar thermal energy is expected to emerge as an important source of renewable energy for meeting the ever-increasing energy requirements of the world. In this regard, there is an increasing demand for spectrally selective coatings for mid- and high- temperature solar thermal applications. In this article, we have reviewed the state-of-the-art of the physical vapor deposited solar selective coatings for mid- and high- temperature solar thermal applications. A variety of physical vapor deposition processes (such as evaporation, ion plating, cathodic arc evaporation, pulsed laser deposition and sputtering) have been used to develop mid- and high- temperature solar selective coatings. Among these, the sputtering technique has been used successfully to deposit these coatings on large area substrates such as flat-plate collectors and receiver tubes and have been commercialized widely. A large variety of solar selective coatings have been

explored and many novel coatings have been prepared in recent years to meet the requirements of mid- and high- temperature applications.

For mid- temperature applications, PVD coatings such as: SS-AlN, CrN-Cr_2O_3, eta Plus, TiNOX, Al-AlN, Ni-NiO, a-C:H/Cr, etc. have been developed and are being commercially used for solar hot water applications. Like electrodeposited black chrome, sputter deposited Cr-Cr_2O_3 coating holds a great promise for solar hot water and mid- temperature applications but needs to be developed on commercial scales as it eliminates the use of hexavalent Cr ions, which are known carcinogen. Similarly, for high- temperature applications, a large number of solar selective coatings such as: Pt-Al_2O_3, Ni-Al_2O_3, Ni-SiO_2, Fe-Al_2O_3, Cr-SiO, Mo-Al_2O_3, Mo-SiO_2, W-Al_2O_3, etc. have been developed. Even though, various researchers have studied Pt-Al_2O_3 coatings for high- temperature applications because of their high absorptance and low emittance at higher operating temperatures, these coatings could not be commercialized due to the high cost of platinum. As an alternative to Pt-Al_2O_3, researchers have developed W-Al_2O_3, Mo-Al_2O_3, Ni-Al_2O_3, etc. cermet coatings for high- temperature applications. The Mo-Al_2O_3 coatings have been used in the Luz receiver tubes which were used for solar thermal power plants. Although, these coatings have good thermal stability in vacuum, they have low thermal stability (≤300°C) in air. Siemens, Germany (formerly Solel) have modified the Mo-Al_2O_3 cermet coating and developed a novel Al_2O_3 based cermet coatings for their receiver tubes, which exhibit higher thermal stability. In addition, W-Al_2O_3 based cermet coatings are also being successfully produced commercially, which are reported to stable up to 550°C in vacuum. Cermet coatings based on other dielectric materials such as SiO_2, AlN and MgO have also been developed. For example, Mo-SiO_2 and SS-AlN cermet coatings have been successfully commercialized for receiver tubes by ENEA and TurboSun, respectively. Even though, the

cermet based coatings exhibit high thermal stability in vacuum, their performance deteriorates significantly when exposed to air due to oxidation and/or diffusion of the metal component in the dielectric matrix. Therefore, recent research has been focused towards the development of high-temperature solar selective coatings based on transition metal nitrides/oxynitrides/oxides and silicides. However, these coatings need to be commercialized for applications in receiver tubes to be used for solar thermal power generation.

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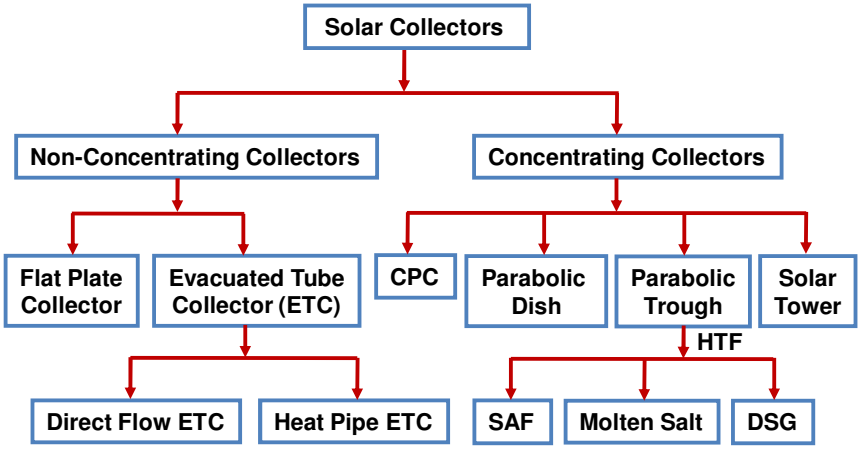
Fig. 1



CPC – Compound Parabolic Concentrator; SAF – Synthetic aromatic fluid;
DSG – Direct steam generation; HTF – Heat transfer fluid

Figure 1: Types of solar collectors.

Fig. 2

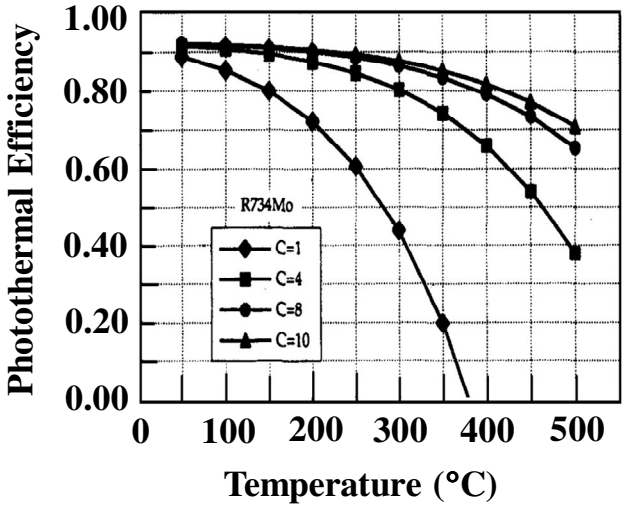


Figure 2: Temperature dependence of the photothermal conversion efficiency at four different concentrations of Co-Al_2O_3 cermet coatings (Reprinted with permission from Ref. 75).

Fig. 3

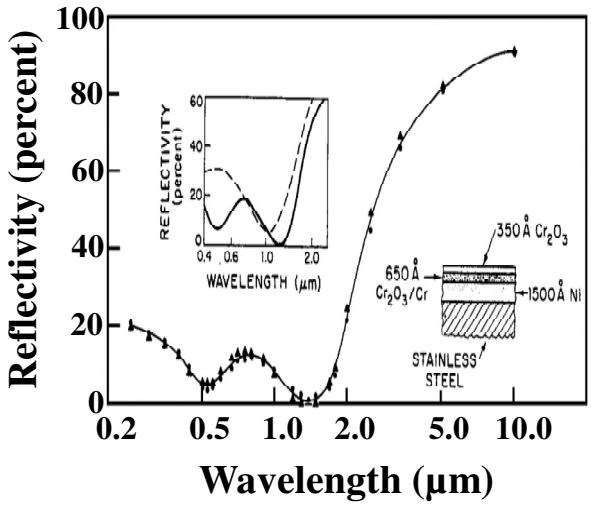


Figure 3: Measured reflectivities of as-deposited (•) and heat-treated Cr_2O_3/Cr cermets (▲) on stainless steel substrates (Reprinted with permission from Ref. 40).

Fig. 4

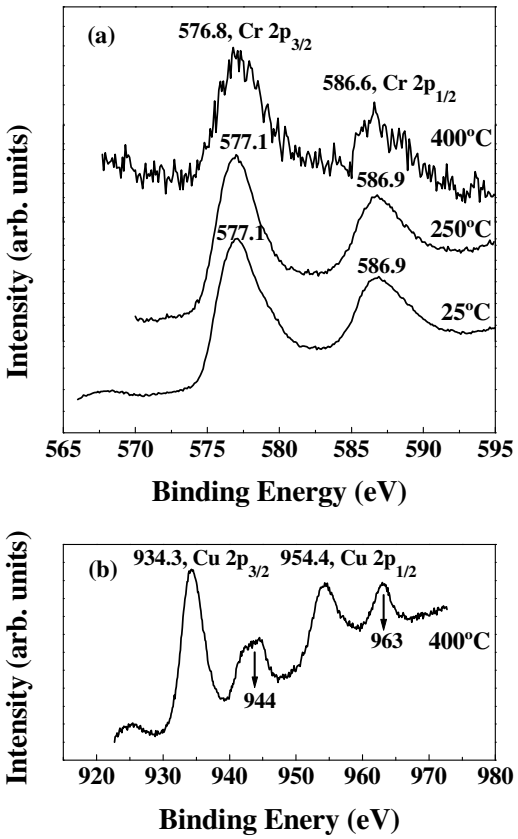


Figure 4: Core level XPS spectra of as-deposited and heat-treated $Cr_xO_y/Cr/Cr_2O_3$ coatings: (a) Cr 2*p* peak and (b) Cu 2*p* peak (Reprinted with permission from Ref. 83).

Fig. 5

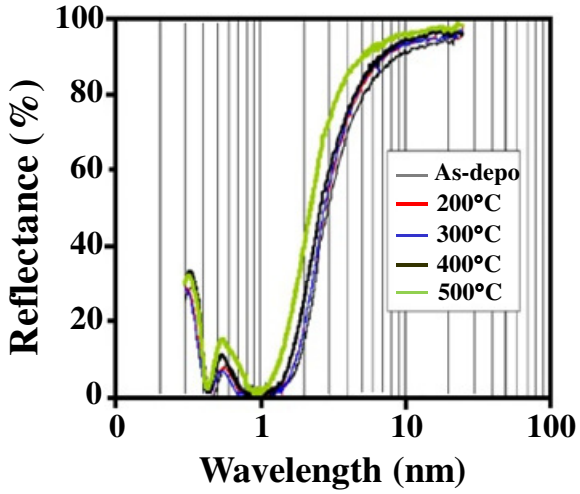


Figure 5: Reflectance spectra of Cr-Cr_2O_3 cermets as a function of annealing temperature (Reprinted with permission from Ref. 84).

Fig. 6

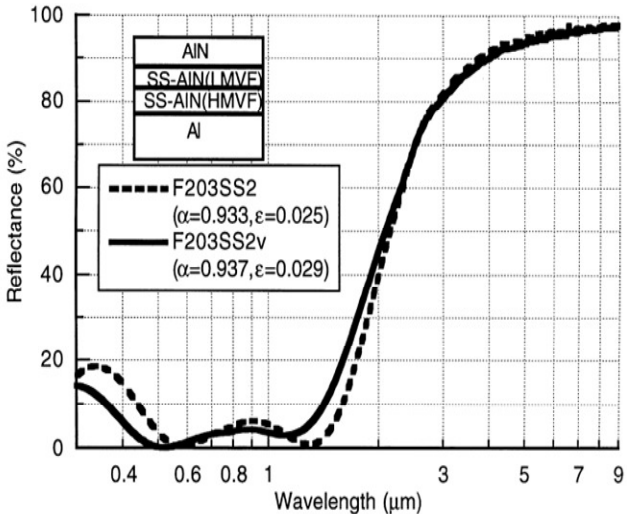


Figure 6: Reflectance spectra of as-deposited (dashed line) and heat-treated (solid line) SS-AlN coatings at 500°C for 1 h (Reprinted with permission from Ref. 114).

Fig. 7

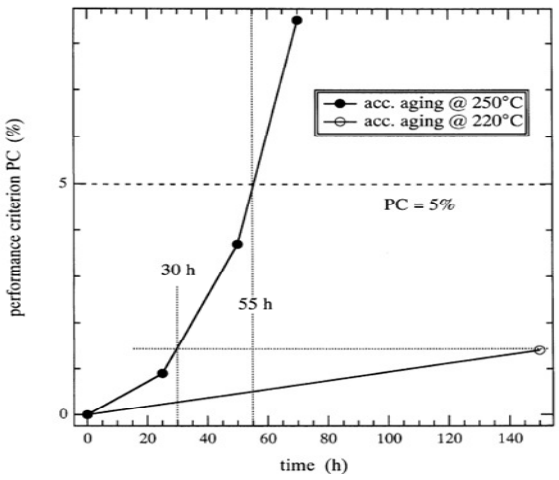


Figure 7: Evolution of performance criterion of a-C:H/Ti coating during accelerated aging tests at 220°C and 250°C. The solid lines illustrate the interpolations between data points, the dashed ones the allowed maximum value for the performance criterion (5%) and the dotted ones the estimations made in the text (Reprinted with permission from Ref. 134).

Fig. 8

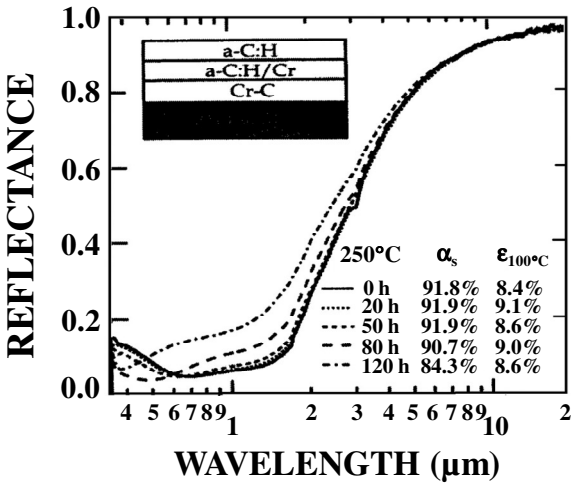


Figure 8: Total reflectance spectra of an a-C:H-Cr absorber coating before and after heat-treatment at 250°C in air for 20, 50, 80 and 120 h. Also shown is the spectrum of as-deposited a-C:H-Cr absorber coating (Reprinted with permission from Ref. 110).

Fig. 9

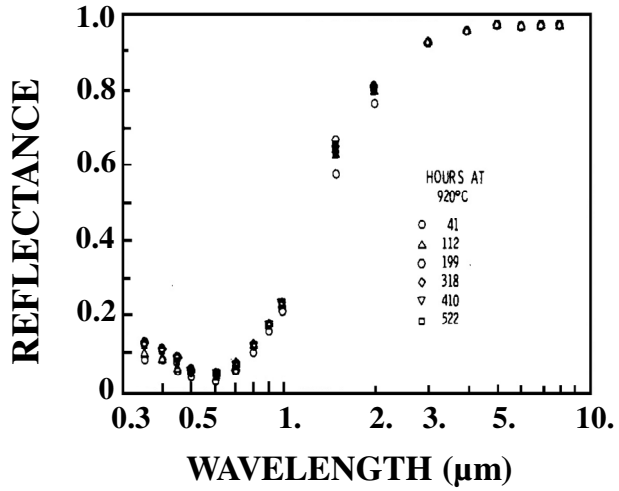


Figure 9: Spectral reflectance of an AMA coating on Mo substrates at 920°C for various durations (Reprinted with permission from Ref. 141).

Fig. 10

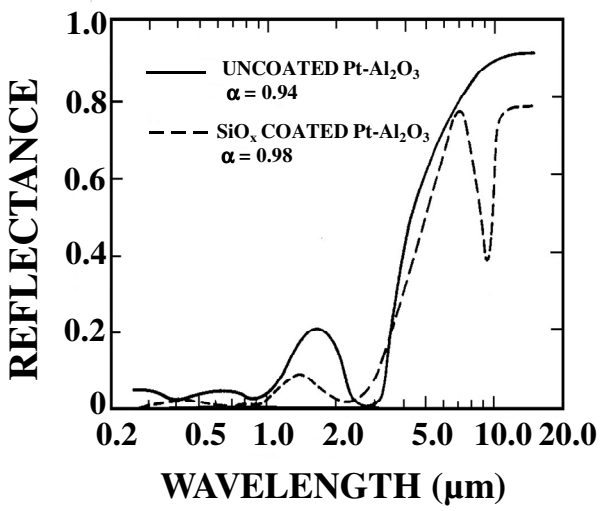


Figure 10: Reflectance spectra of Pt-Al_2O_3 cermet (–) without SiO_x antireflection coating and (----) with SiO_x antireflection coating (Reprinted with permission from Ref. 144).

Fig. 11

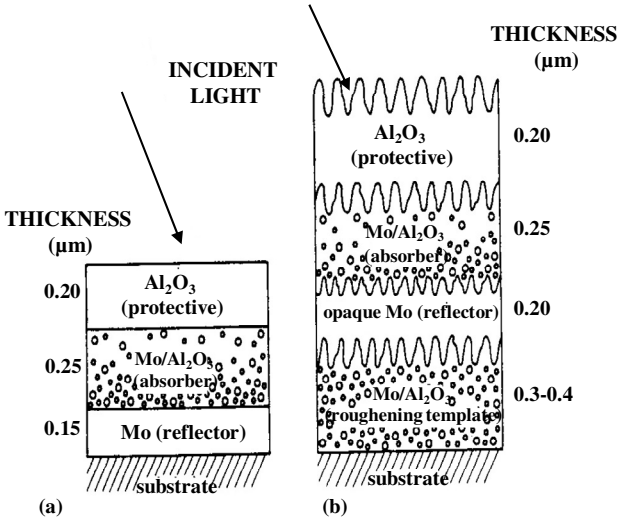


Figure 11: Cross-sectional schematic of two types of Mo/Al_2O_3 cermets: (a) standard graded-index cermet (b) modified design (Reprinted with permission from Ref. 146).

Fig. 12

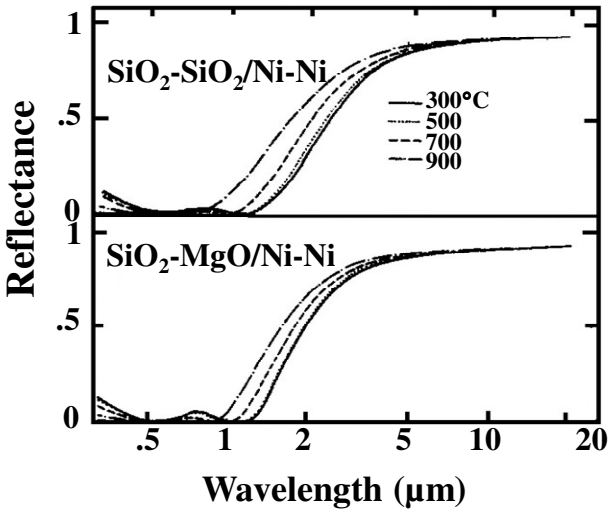


Figure 12: Reflectance spectra of Ni-SiO_2 and Ni-MgO cermet coatings at different operating temperatures (Reprinted with permission from Ref. 151).

Fig. 13

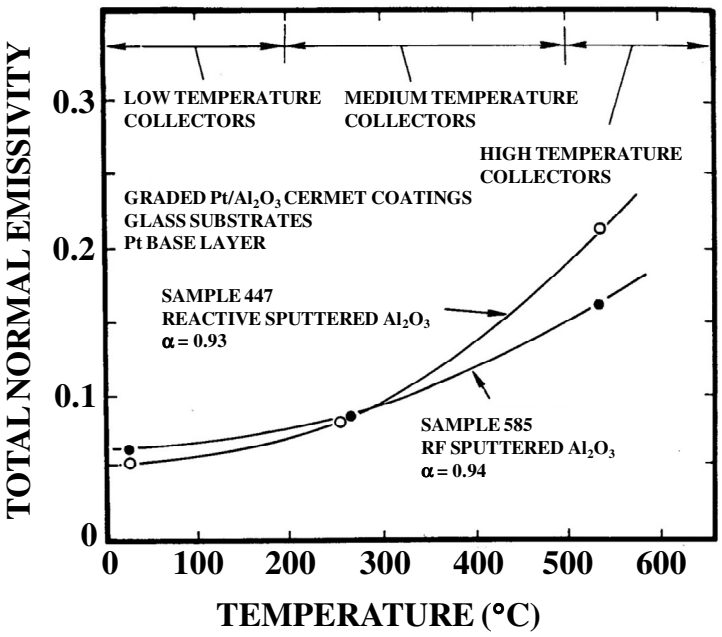


Figure 13: Temperature dependence of normal emittance for graded Pt-Al_2O_3 cermet coatings with Pt IR reflection layers (Reprinted with permission from Ref. 154).

Fig. 14

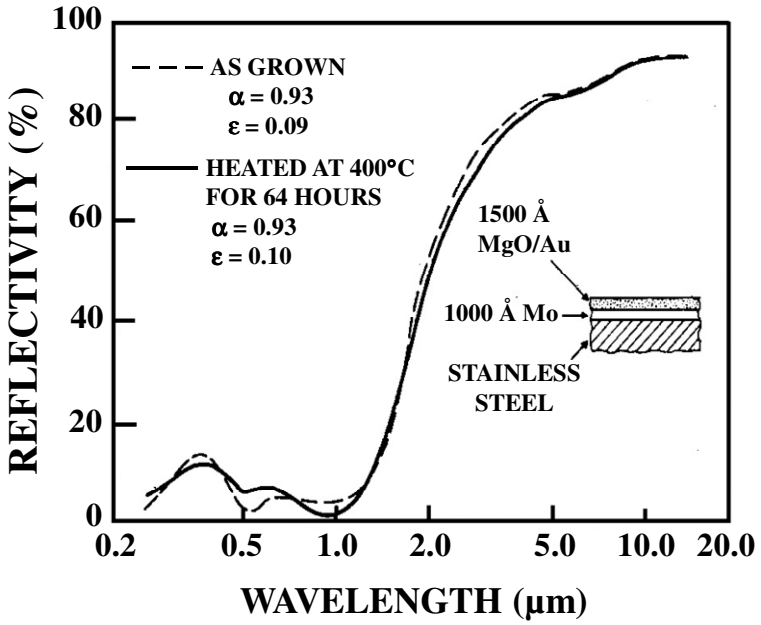


Figure 14: Reflectance spectra of as-deposited and heat-treated Au/MgO cermets on molybdenum coated stainless steel (Reprinted with permission from Ref. 150).

Fig. 15

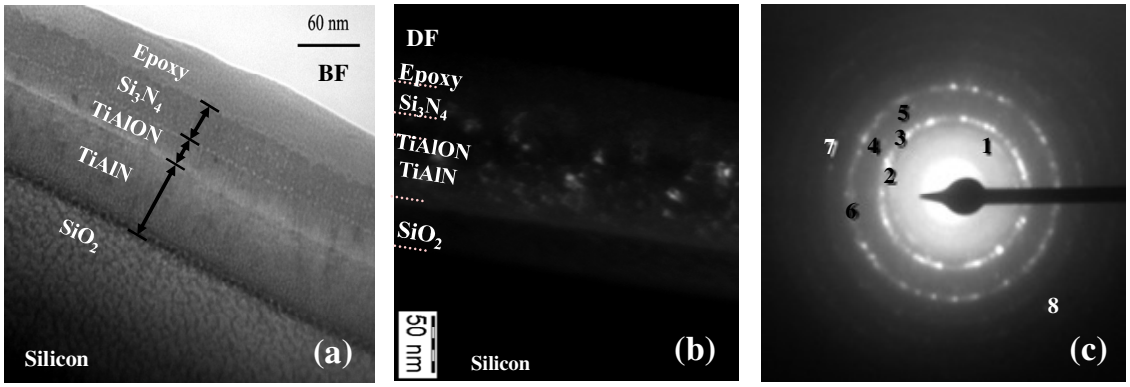


Figure 15: Cross-sectional view of TiAlN/TiAlON/Si_3N_4 tandem absorber deposited on Si substrate: (a) bright-field TEM image, (b) dark-field TEM image and (c) selective area diffraction pattern (Reprinted with permission from Ref. 180).

Fig. 16

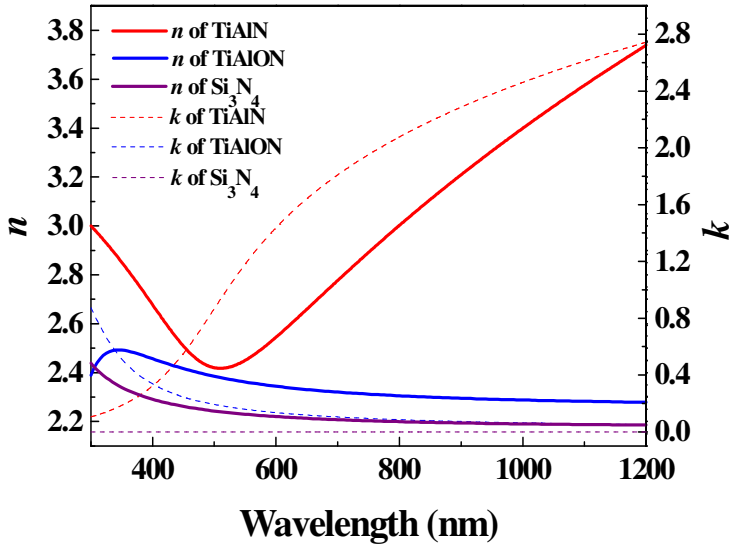


Figure 16: Experimentally determined '*n*' and '*k*' values of the TiAlN/TiAlON/Si_3N_4 tandem absorber deposited on Cu substrate (Reprinted with permission from Ref. 178).

Fig. 17

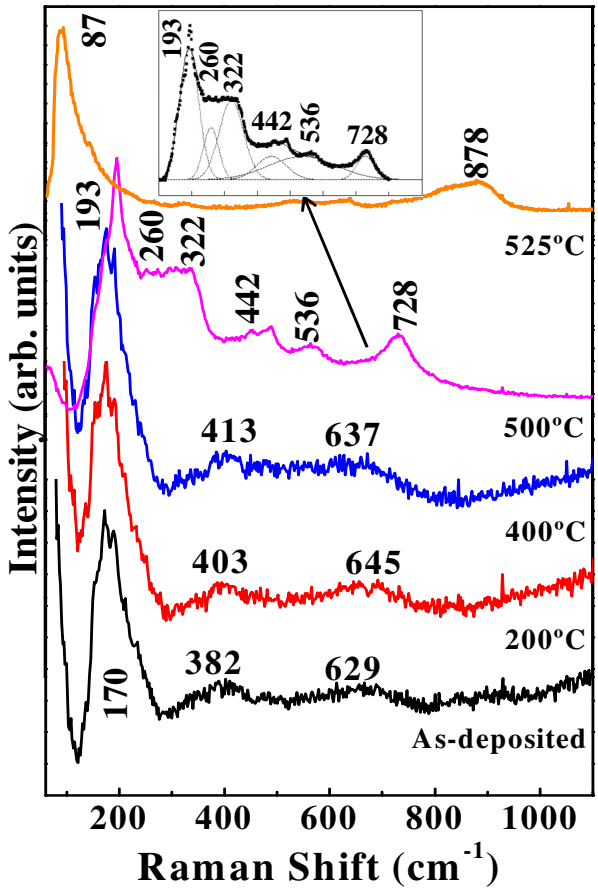


Figure 17: Composite Raman spectra of as-deposited $Mo/HfO_x/Mo/HfO_2$ coating on Cu substrate and coatings heat-treated up to 525°C for 2 h in air. Also shown in the inset is the deconvoluted Raman spectrum of coating heat-treated at 500°C (Reprinted with permission from Ref. 173).

Fig. 18

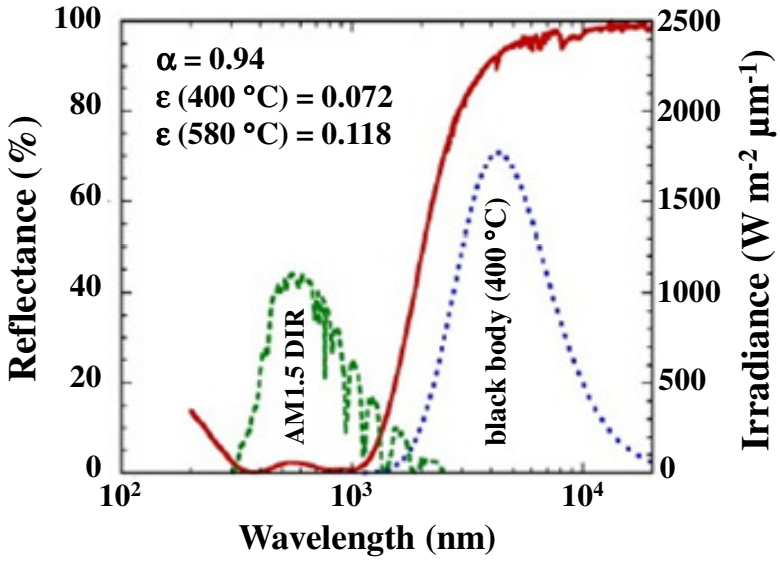


Figure 18: Experimental reflectance spectra (–) and corresponding photo-thermal parameters for an optimized Mo-SiO_2 cermet coating. In the graph, the direct AM 1.5 solar spectrum and the ideal blackbody emission (T = 400°C) are also reported (Reprinted with permission from Ref. 167).